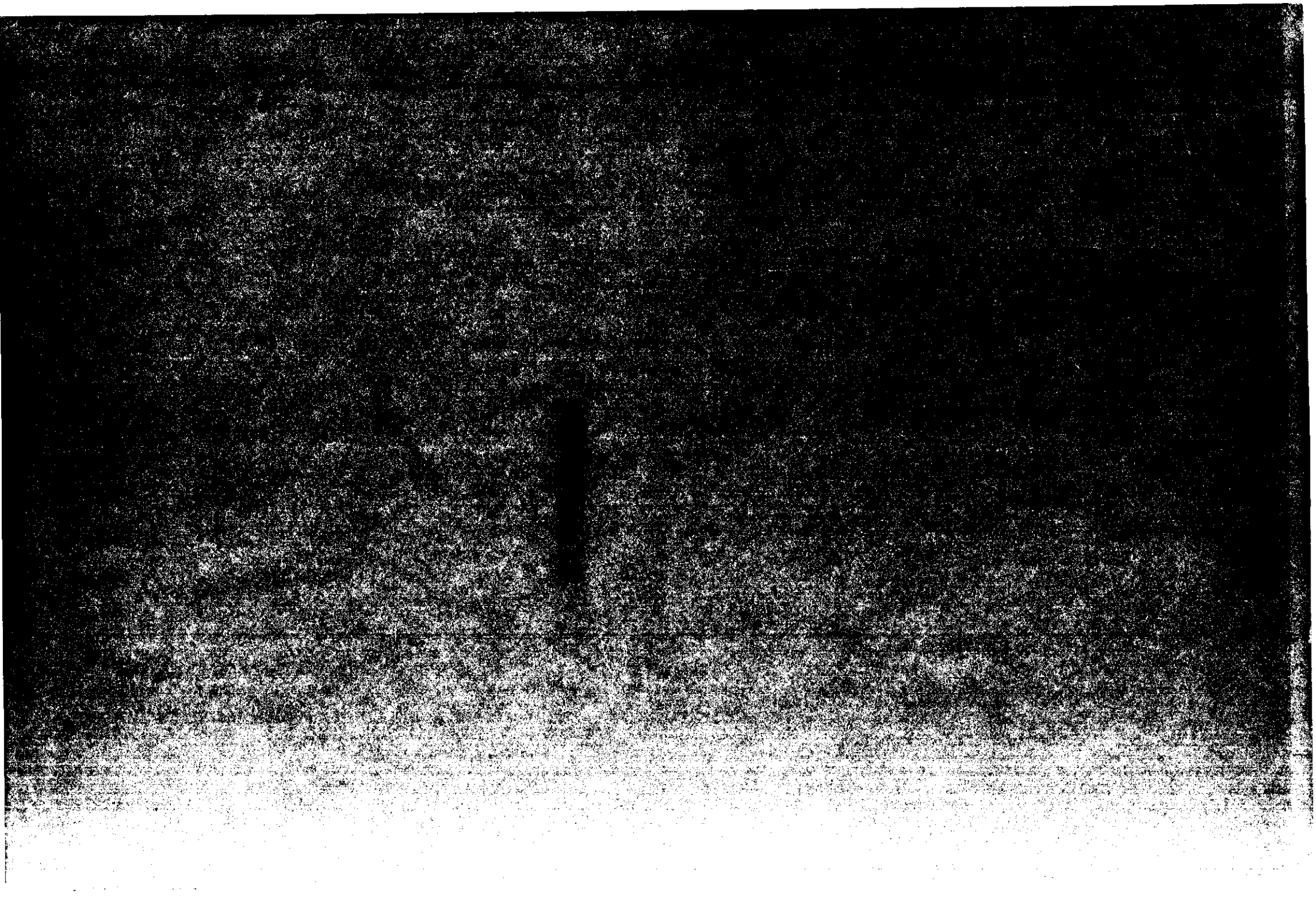

SUMMARY

In the present work, acrylic and methacrylic esters of N-hydroxyphthalimide were synthesized and polymerized. The synthesis of N-acryloyloxy- and N-methacryloyloxyphthalimides were accomplished in fair yield by the reaction of acryloyl and methacryloyl chlorides with N-hydroxyphthalimide in the presence of triethylamine. Also, N-acryloyloxy- and N-methacryloyloxyphthalimide monomers were prepared from the reaction of acrylic and methacrylic acids with N-hydroxyphthalimide in the presence of N,N-dicyclohexylcarbodiimide. The prepared monomers were polymerized by solution polymerization and the polymers were collected by filtration, washed and dried. The ability of the prepared activated polymers to enter an exchange reactions with amines (ethylamine, piperidine and p-anisidine) and alcohols (phenol and cyclohexanol) and the percent exchange reactions were almost quantitative as indicated by elemental and spectrophotometric analyses.

Similarly, methacrylic ester of N-hydroxytetrabromophthalimide was synthesized and polymerized. The synthesis of N-methacryloyloxytetrabromophthalimide was carried out by the reaction of methacryloyl chloride with N-hydroxytetrabromophthalimide in presence of triethylamine, and also, from the reaction of methacrylic acid with N-hydroytetrabromophthalimide in presence

of N,N-dicyclohexylcarbodiimide as dehydrating agent. The exchange ability of the prepared poly-N-methacryloyloxytetrabromophthalimide with amines and amino acids was calculated from bromine analysis and the percent exchange was found to be: 85.75, 88.24, 92.52, 72.11 and 75.11 % for aniline, p-toluidine, p-anisidine, o-aminobenzoic acid and p-aminobenzoic acid, respectively. The percent exchange reaction of poly-N-methacryloyloxytetrabromophthalimide with hydroxylated compounds was also studied and calculated from bromine analysis and was found to be: 84.09, 84.19, 61.61 and 67.08 % for phenol, cyclohexanol, o-hydroxybenzoic acid and p-hydroxybenzoic acid, respectively.

Also, a direct comparison between the exchange reactions of poly-N-methacryloyloxyphthalimide and poly-N-methacryloyloxytetrabromophthalimide with p-anisidine (as an example of amines) and cyclohexanol (as an example of hydroxylated compounds) was carried out at various times (15-120 min.) at 60°C, and the percent exchange reaction in each case was calculated from ^{1}H NMR spectroscopy and elemental analysis. The results indicate that the percent exchange reactions of p-anisidine with both polymers was almost the same at various times of reaction, while in case of cyclohexanol the percent exchange reactions with poly-N-methacryloyloxytetrabromophthalimide were much higher than those with poly-N-methacryloyloxyphthalimide.

Copolymerization reactions of N-acryloyloxyphthalimide (NAP) and N-methacryloyloxyphthalimide (NMP) with methyl acrylate (MA), methyl methacrylate (MMA) and acrylonitrile (AN) were studied and the copolymer composition for each sample was calculated from ^1H NMR spectroscopy. The monomer reactivity ratios for the systems studied were determined according to the Fineman-Ross and Kelen-Tüdős methods as illustrated in the following Table:

system	Fineman-Ross method		Kelen-Tüdős method	
M_1-M_2	r_1	r_2	r_1	r_2
NAP-MA	0.922	1.146	0.961	1.164
NAP-MMA	0.292	1.799	0.297	1.811
NAP-AN	1.124	1.336	1.051	1.289
NMP-MA	1.147	0.170	1.223	0.208
NMP-MMA	1.370	0.641	1.441	0.704
NMP-AN	1.400	0.223	1.496	0.228

The r_1r_2 values for NAP-MMA, NMP-MA and NMP-AN systems (0.540, 0.254 and 0.341, respectively) indicate that the copolymers in both cases should have a random distribution of the monomer units, while for the NAP-MA, NAP-AN and NMP-MMA systems, the r_1r_2 values (1.120, 1.34 and 1.014, respectively) illustrate a low tendency of the monomers to alternate and the copolymer should be composed mainly of small sequences of monomeric units of the same type. In all systems studied no azeotropic copolymers appear.

Also, in the present investigation, four terpolymer systems involving NAP or NMP with AN and MA or MMA were prepared. A computer program based on the terpolymer-composition equation was used to facilitate the calculations of the ternary monomer-polymer composition relationship. In all cases no ternary azeotropies appear. Selective feed compositions corresponding to unitary and binary azeotropies for each terpolymer system were polymerized to low conversions. The experimental terpolymer compositions agreed well with the predicted values which indicate the correctness of the determined monomer reactivity ratio values. It was concluded that the free radical terpolymerization reactions of the systems studied followed the classical copolymerization theory.

PUBLICATIONS FROM THE PRESENT WORK

Parts of the present work have been subsequently published and are listed below as follows:

1- Poly-N-acryloyloxy- and -N-methacryloyloxyphthalimides as activated drug-binding matrices.
A.F. Shaaban, M.M.H. Arief, A.A. Khalil and N.N. Messiha.
Acta Polymerica, 39, 145 (1988).

2- Binary copolymerizations of N-acryloyloxyphthalimide with methyl acrylate, methyl methacrylate and acrylonitrile.
A.F. Shaaban, A.A. Khalil and N.N. Messiha.
Acta Polymerica 40, 445 (1989).

3- Estimation of Reactivity Ratios of N-Methacryloyloxyphthalimide Copolymers by ^{1}H NMR.
A.F. Shaaban, A.A. Khalil and N.N. Messiha.
J. Appl. Polymer Sci. 37, 2051 (1989).

Poly-N-acryloyloxy- and -N-methacryloyloxyphthalimides as activated drug-binding matrices

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The synthesis of N-acryloyloxy- and N-methacryloyloxyphthalimides were accomplished in fair yield by reaction of acryloyl and methacryloyl chlorides with N-hydroxyphthalimide in the presence of triethylamine. The resulting monomers were polymerized. The ability of the prepared activated polymers to enter exchange reactions with hydroxylated compounds and amines was tested.

Poly-N-acryloyloxy- und -N-methacryloyloxyphthalimide als aktivierte Matrix zur Fixierung von Pharmaka

N-Acryloyloxy- und N-Methacryloyloxyphthalimide wurden durch die Reaktion der Acryloyl- und Methacryloylchloride mit N-hydroxyphthalimid in Gegenwart von Triethylamin in guter Ausbeute synthetisiert. Die Monomere wurden polymerisiert. Die Eignung der so erhaltenen aktivierten Polymere für Austauschreaktionen mit Aminen und Hydroxylverbindungen wurde untersucht.

Поли-N-акрилоилокси- и -N-метакрилоилоксифталимиды в качестве активированной матрицы для фиксации лечебных веществ

N-Акрилоилокси- и -*N*-метакрилоилоксифталимиды с хорошим выходом были получены реакцией акрилоил- и метакрилоилхлоридов с *N*-гидроксифталимидом в присутствии триэтиламина. Затем эти мономеры полимеризировались. Была исследована возможность применения полученных активированных полимеров для реакции обмена с аминами и гидроксильными соединениями.

1. Introduction

One of the most interesting topics in the field of pharmacologically active polymers is the preparation of polymeric drugs in which drugs are attached to the polymeric backbone via covalent bonds with limited stability to biological environments [1, 2]. If the drug molecule contains hydroxy or amino groups, the polymeric drugs are best prepared by reacting the drug with the presynthesized polymer with functional side groups able to react selectively with the above groups, giving ester or amido bonds [1, 3]. Several activated esters and amides of acrylic and methacrylic acids and their polymers have been described [4—7]. The aim of the present work is to find the optimal general conditions for the synthesis and polymerization of some new monomeric phthalimides as well as the exchange reactions of their polymers with some aminated and hydroxylated model compounds.

2. Experimental

2.1. Synthesis

N-acryloyloxy- (IV) and N-methacryloyloxyphthalimides (V) were prepared as follows: To a well-stirred cold solution (0 to 5°C) of N-hydroxyphthalimide (0.2 mol), triethylamine (0.2 mol) in 250 ml dry chloroform, acryloyl or methacryloyl chloride (0.2 mol) was added dropwise. The reaction mixture was then allowed to stand at room temperature for 2 h and poured in excess petroleum ether (40 to 60°C) to reprecipitate the triethylamine hydrochloride. After filtration the filtrate was extracted with water to remove any residual triethylamine hydrochloride, and evaporated to dryness in vacuo. The residue was recrystallized from benzene/petroleum ether (20/80). The yields of recrystallized products usually ranged from 87 to 93%. mp = 118···120°C and 112···114°C for monomers IV and V, respectively. (All melting points are uncorrected.)

Anal.: Calc. for IV ($C_{11}H_7NO_4$): C, 60.82%; H, 3.22%; N, 6.45%.
Found: C, 60.64%; H, 3.36%; N, 6.40%.
Calc. for V ($C_{12}H_9NO_4$): C, 62.33%; H, 3.89%; N, 6.06%.
Found: C, 61.82%; H, 3.80%; N, 6.04%.

2.2. Polymerization

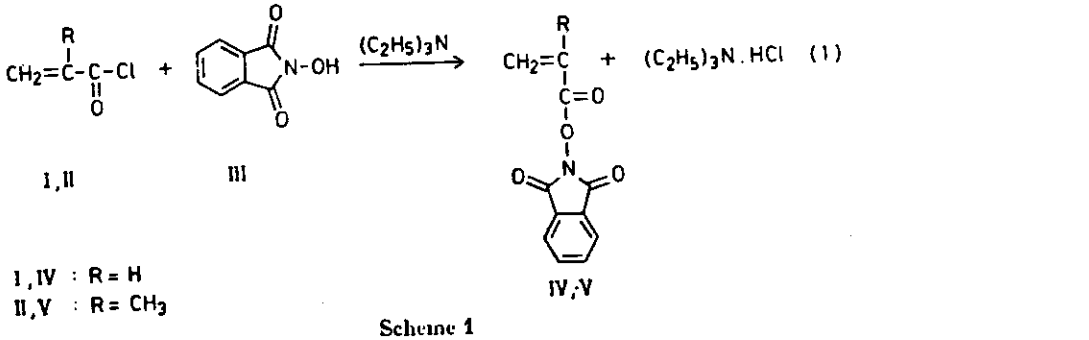
Solutions (20%) of the monomers in dimethylformamide (DMF) were treated with azobisisobutyronitrile (AIBN) (1 mole-%). After purging with deoxygenated nitrogen, the reaction mixture was allowed to stand at 60°C for 6 h. The polymers (VI and VII) were obtained by reprecipitation in methanol, and were collected by filtration, washed, dried and weighed. The yields are 86 and 95% for polymers VI and VII, respectively.

2.3. Exchange reactions

To a 10% solution of polymer in DMF 2 equivalents of amine was added. The reaction mixture was allowed to stand at 60°C for 6 h. Similarly, the exchange reaction with hydroxylated compounds were carried out except that the triethylamine (2 equivalents) was also added to the reaction mixture. In all cases, the products were isolated by pouring the reaction mixture into an excess of diethyl ether, filtering, dissolving in DMF, reprecipitating with diethyl ether and drying.

2.4. Spectrometry

IR spectra were run on a Unicam SP-1200 spectrophotometer. ^{1}H NMR spectra were measured on a 90 MHz Varian EM-390 spectrometer in deuterated dimethylsulfoxide (DMSO) with tetramethylsilane as the internal standard.



Scheme 1

Table 1. IR and ^{1}H NMR spectra of monomers IV and V and their polymers VI and VII

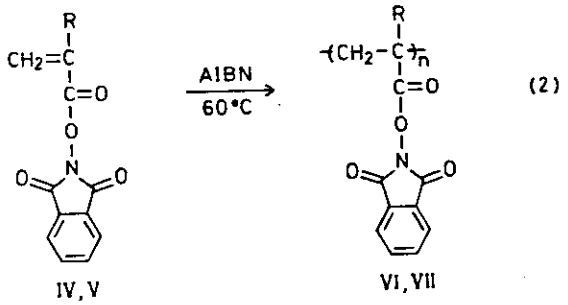
Compound	IR spectra $\nu_{C=O}$ (ester) cm^{-1}	IR spectra $\nu_{C=O}$ (cyclic imide) cm^{-1}	IR spectra $\nu_{C=C}$ cm^{-1}	^{1}H NMR spectra Segment	^{1}H NMR spectra Chemical shift ppm
IV	1735	1840, 1790	1625	CH_2=CH–	6.1···6.9
				–C_6H_4–	7.9
V	1735	1835, 1795	1625	CH_2=C–	5.9, 6.5
				–CH_3	2.1
				–C_6H_4–	7.9
VI	1735	1810, 1785	–	–CH_2–CH–	1.0···1.9
				–C_6H_4–	7.9
VII	1735	1805, 1780	–	–CH_2–, –CH_3	0.8···2.1
				–C_6H_4–	7.9

3. Results and discussion

3.1. Polymerization

The monomers described in this work have been prepared in fair yields by reaction of the acid chlorides (I and II) with N-hydroxyphthalimide (III) in the presence of triethylamine (equation (1), Scheme 1 see p. 145). The monomers were a white crystalline solid, easily soluble in most organic solvents, but sparingly soluble in aliphatic hydrocarbons such as n-hexane and petroleum ether.

The monomers were readily polymerized in solution with AIBN as a free radical initiator. The polymers VI and VII are soluble in cold DMF and DMSO but insoluble in water and most organic solvents.



Scheme 2

The structure of the monomers and polymers were established from IR and ^{1}H NMR spectra (Table 1).

3.2. Reactions of the polymers with amines

The ability of polymers VI and VII to enter an exchange reaction with amines were tested with ethylamine, piperidine and p-anisidine. In a typical experiment, a 10% solution of polymer VI or VII in DMF was treated with 2 equivalents of amine (equation (3)), and the reaction mixture was allowed to stand at 60°C for 6 h (Scheme 3).

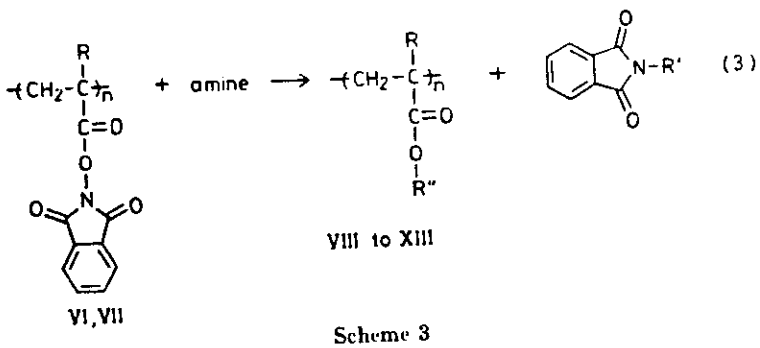
VIII: R = H; R′ = C_2H_5; R″ = C_2H_5NH
IX: R = CH_3; R′ = C_2H_5; R″ = C_2H_5NH
X: R = H; R′ = OH; R″ = $C_5H_{10}N$
XI: R = CH_3; R′ = OH, R″ = $C_5H_{10}N$
XII: R = H; R′ = p-CH_3O–C_6H_4; R″ = p-CH_3O–C_6H_4–NH
XIII: R = CH_3; R′ = p-CH_3O–C_6H_4; R″ = p-CH_3O–C_6H_4–NH

The yield of the exchange reaction was calculated from nitrogen analysis. In all cases the exchange reaction was almost practically quantitative (Table 2). This was confirmed by IR spectroscopy. In the spectra of compounds VIII to XIII the bands at about 1735 and 1785, 1810 cm^{-1}, present in the spectra of polymers VI and VII, which are attributed to $\nu_{C=O}$ of ester and cyclic imides, respectively, entirely disappeared after the exchange reaction. At the same time, new strong bands at about 1630···1640 cm^{-1} and 1510···1530 cm^{-1} assigned to $\nu_{C=O}$ (amide I and II), respectively, appeared.

This was also confirmed by ^{1}H NMR spectroscopy. Table 3 illustrates the ^{1}H NMR data of the exchange reactions of poly-N-acryloyloxy- and -N-methacryloyloxyphthalimides with amines. From Tables 2 and 3 it is

Table 2. Exchange reactions of polymers VI and VII with amines

Polymer	Co-reactant	N Calc. for 100% exchange %	N Found %	Exchange %
VI	Ethylamine	14.14	11.25	79
	Piperidine	10.07	10.10	100
	p-Anisidine	7.90	7.80	92
VII	Ethylamine	12.39	12.02	92
	Piperidine	9.15	8.15	86
	p-Anisidine	7.33	7.44	100



Scheme 3

Table 3. ^1H NMR spectral data of the exchange reactions of polymers VI and VII with amines

Exchange products	Segments	Chemical shift ppm	Exchange %
VIII	CH_3-, CH_2-C-, $-C-CH-$ $-CH_2N-$ $-C_6H_4-$[1] $-NH-$	1.1, 1.5, 2.1 3.1 7.9 5.5	81
IX	CH_3-C-, $-CH_2-C-$ $-CH_2-N-$ C_6H_4-[1] $-NH-$	1.0, 1.75 3.0 7.9 6.0	95
X	$-(CH_2)_3-$, $-CH_2-CH-$ $-CH_2-N-CH_2-$ $-C_6H_4-$[1]	1.5 (broad) 3.3 7.9	97
XI	CH_3-C-, $-(CH_2)_3-$; CH_2-C- $-CH_2-N-CH_2-$ $-C_6H_4-$[1]	1.2, 1.8 3.3 7.9	87
XII	$-CH_2-CH-$ $-OCH_3$ $-C_6H_4-$ $-C_6H_4-$[1] $-NH-$	1.5 (broad) 3.65 6.5···7.5 7.9 5.7	90
XIII	CH_3-C-, $-CH_2-C-$ $-OCH_3$ $-C_6H_4-$ $-C_6H_4-$[1] $-NH-$	1.1, 1.9 3.7 6.4···7.7 7.9 6.0	95

[1] Due to the unexchanged phthalimide residues

Table 4. ^1H NMR spectral data of the exchange reactions of polymers VI and VII with hydroxyl compounds

Exchange products	Segments	Chemical shift ppm	Exchange %
XIV	$-CH_2-CH-$ C_6H_5-	1.0···2.3 6.7···7.8	100
XV	CH_3-C-CH_2- C_6H_5-	0.7···2.3 6.6···7.7	100
XVI	$(CH_2)_5-$, CH_2-CH- $-CH-O-$ $-C_6H_4-$[1]	1.0···2.3 4.6 7.9	89
XVII	CH_3-C-CH_2-, $-(CH_2)_5-$ $-CH-O-$ $-C_6H_4-$[1]	0.7···2.2 4.6 7.9	92

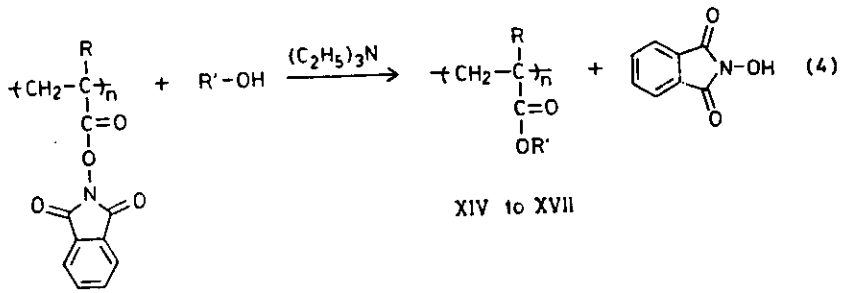
[1] Due to the unexchanged phthalimide residues.

seen that the yields of the exchange reactions calculated from nitrogen analysis are in agreement with those obtained from ^1H NMR spectroscopy.

3.3. Reactions of the polymers with hydroxyl compounds

The ability of polymers VI and VII for exchange reactions with hydroxyl compounds was tested with phenol and cyclohexanol (equation (4), Scheme 4).

Nitrogen was absent in all exchange products. This means that the exchange reactions were almost practically quantitative. This was also confirmed by ^1H NMR spectroscopy (Table 4) for the exchange products of both polymers with phenol and cyclohexanol. It was observed that cyclohexanol is less reactive than phenol. These results are in agreement with the results obtained by FERRUTI et al. [7]. They reported that cyclohexanol is



VI, VII

XIV to XVII

XIV : R = H; R' = C_6H_5
XV : R = CH_3, R' = C_6H_5
XVI : R = H; R' = C_6H_{11}
XVII : R = CH_3; R' = C_6H_{11}

Scheme 4

less reactive than phenol and methanol when reacted with 1-methacryloyl benzotriazoles in the presence of triethylamine.

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Binary copolymerizations of N-acryloyloxyphthalimide with methyl acrylate, methyl methacrylate and acrylonitrile

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N-Acryloyloxyphthalimide was prepared by the reaction of acrylic acid with N-hydroxyphthalimide in the presence of N,N'-dicyclohexylcarbodiimide. The monomer reactivity ratios for the copolymerization of N-acryloyloxyphthalimide with methyl acrylate, methyl methacrylate, and acrylonitrile, respectively, were estimated by ^{1}H-NMR spectroscopy. The copolymer compositions were determined from ^{1}H-NMR spectroscopic data. The Q and e values for N-acryloyloxyphthalimide were calculated.

Binäre Copolymerisation von N-Acryloyloxyphthalimid mit Methylacrylat, Methylmethacrylat und Acrylnitril

N-Acryloyloxyphthalimid wurde durch die Reaktion von Acrylsäure mit N-Hydroxyphthalimid in Gegenwart von N,N'-Dicyclohexylcarbodiimid synthetisiert. Die Reaktivitätsverhältnisse der Monomere für die Copolymerisation von N-Acryloyloxyphthalimid mit Methylacrylat, Methylmethacrylat und Acrylnitril sowie die Zusammensetzung der Copolymere wurden mit Hilfe der ^{1}H-NMR-Spektroskopie ermittelt. Die Q- und e-Werte für N-Acryloyloxyphthalimid wurden berechnet.

Бинарная сополимеризация N-акрилоилоксифталимида с метилакрилатом, метилметакрилатом и акрилонитрилом

N-Акрилоилоксифталимид синтезировался из акриловой кислоты и N-гидроксифталимида в присутствии N,N'-дициклогексилкарбодиимида. Было определено соотношение реактивности мономеров для сополимеризации с метилакрилатом, метилметакрилатом и акрилонитрилом, а также и состав сополимера определялся с помощью ^{1}H-ЯМР-спектроскопии. Вычислялись значения Q и e для N-акрилоилоксифталимида.

1. Introduction

Activated esters of acrylic and methacrylic acids may be used as precursors of some classes of multifunctional polymers [1]. We have already reported the synthesis and polymerization of the acrylic and methacrylic esters of N-hydroxyphthalimide as well as the ability of the resulting polymers to react with compounds bearing hydroxyl or amino groups [2]. For this reason, they provide a very convenient means for the preparation of some classes of macromolecular drugs. Free radical copolymerization of these activated esters with vinyl monomers is a method of modifying the properties of polymers.

The incorporation of high proportions of active monomers and their better distribution within the polymer chain can be achieved through fundamental studies of the copolymerization parameters under specified reaction conditions. Spectroscopic methods such as ^{1}H-NMR spectroscopy offer a simple and rapid evaluation of copolymer composition [3—5] compared to the other techniques [6, 7]. In recent years, the value of ^{1}H-NMR spectroscopy in the analysis of copolymers and determination of the sequence distribution of monomers has been fully recognized. In the present work, the estimation of monomer reactivity ratios for copolymerizations of N-acryloyloxyphthalimide with methyl acrylate, methyl methacrylate and acrylonitrile from ^{1}H-NMR spectral data are reported.

2. Experimental

N-Acryloyloxyphthalimide (NAP) was prepared by the reaction of acrylic acid with N-hydroxyphthalimide in the presence of N,N-dicyclohexylcarbodiimide (DCCI). To a cooled solution (0 to 5 °C) of 16.3 g (0.1 mol) of N-hydroxyphthalimide and 7.2 g (0.1 mol) of acrylic acid in methylene chloride (50 ml) was added 20.6 g (0.1 mol) of DCCI with stirring. After 4 h stirring at room temperature, the precipitated dicyclohexyl urea was removed by filteration and the filtrate was evaporated to dryness in vacuo. The residue was then recrystallized from benzene, mp. 121 °C (lit. [2] 118—120 °C); yield 18.2 g (83.9%).

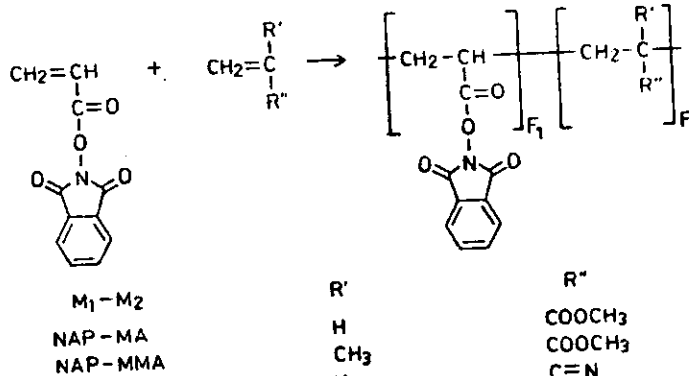
Methyl acrylate (MA), methyl methacrylate (MMA) and acrylonitrile (AN) (E. Merck, Darmstadt, Fed. Rep. Germany) were freed from inhibitors by distillation under reduced pressure and the middle cuts retained for use. Azobisisobutyronitrile (AIBN) was purified by recrystallization from absolute alcohol (mp. 102 °C).

The copolymers were obtained by solution polymerization. Solutions of predetermined amounts of the comonomers in dimethylformamide (1 mol/l) were preheated to the appropriate polymerization temperature (70 °C). The polymerization was commenced by adding AIBN (1 mol %). The copolymers were precipitated by pouring the polymerization mixtures into methanol. After several successive reprecipitations from dimethylformamide into methanol, the samples were washed, dried and weighed. The conversions were kept below 10% in all preparations.

^{1}H-NMR spectra of the copolymer samples (in DMSO-d6 or $CDCl_3$ as a solvent and using TMS as zero reference) were recorded using a Varian EM-390 spectrometer operating at 90 MHz.

3. Results and discussion

In the present investigation the copolymerization of NAP with MA, MMA, and AN is studied, and the reactions can be written as shown in scheme 1.



M_1-M_2	R'	R''
NAP—MA	H	$COOCH_3$
NAP—MMA	CH_3	$COOCH_3$
NAP—AN	H	$C\equiv N$

Scheme 1

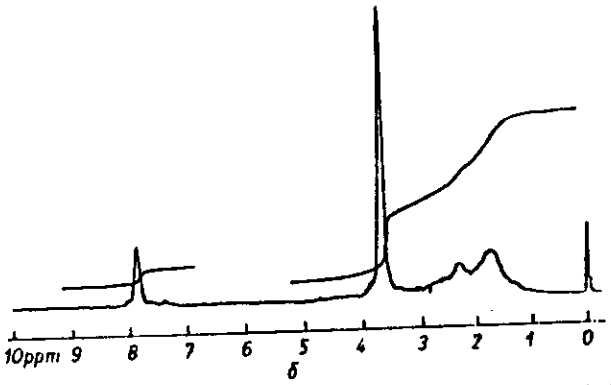


Fig. 1. ^{1}H-NMR spectrum of an NAP-MA copolymer sample in $CDCl_3$ prepared at molar fraction $f_1 = 0.2$

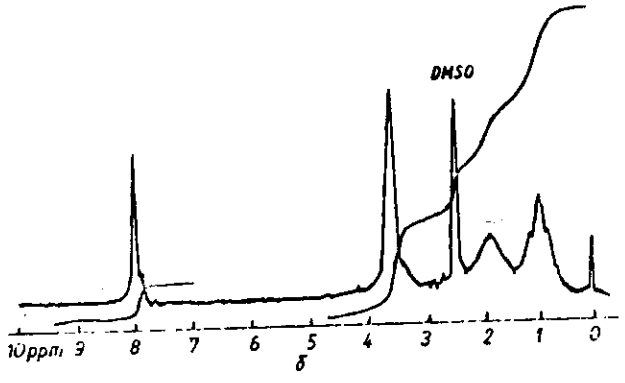


Fig. 2. ^{1}H-NMR spectrum of an NAP-MMA copolymer sample in DMSO-d_6 prepared at molar fraction $f_1 = 0.40$

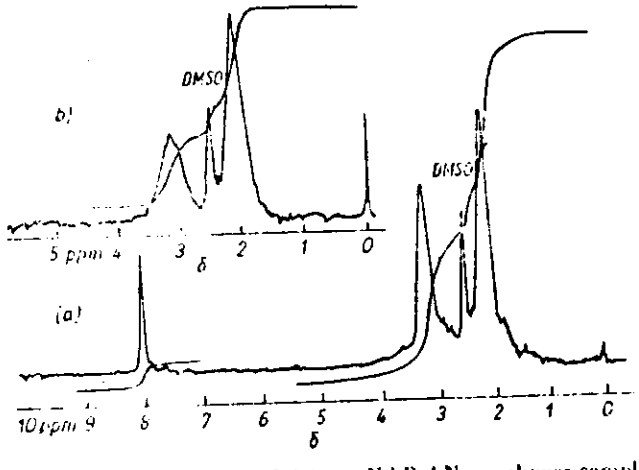


Fig. 3. ^{1}H-NMR spectra of (a) an NAP-AN copolymer sample in DMSO-d_6 prepared at molar fraction $f_1 = 0.10$ and (b) a polyacrylonitrile sample

In all studied systems the distribution of protons is an important factor to distinguish the units in the copolymer chain. The ^{1}H-NMR spectra of NAP-MA copolymers show the following characteristic peaks:

(i) One Peak at $\delta = 7.85$ ppm due to phenyl protons of the NAP units;

(ii) one peak at $\delta = 3.65$ ppm due the methoxy group of the MA units;

(iii) two peaks (broad) in the highest field centered at $\delta = 2.35$ ppm and $\delta = 1.8$ ppm due to the methine and methylene protons, respectively, of both NAP and MA units.

Table 1. Analytical data for copolymerization of NAP with MA

a [1])	Conversion %	b [1])
1.5000	7.3	1.3333
1.0000	6.8	0.9286
0.6667	5.4	0.5833
0.4286	7.9	0.3749
0.2500	8.1	0.2307
0.1111	6.3	0.0978
0.0526	7.4	0.0441

[1]) a — the molar ratio of M_1 and M_2 in the feed, and b — the molar ratio of M_1 and M_2 in the copolymer

Figure 1 shows a typical spectrum of an NAP-MA copolymer sample as an example. The ^{1}H-NMR spectra of NAP-MMA copolymers have similar characteristic peaks except that the highest peak due to the α-methyl protons of the MMA unit is centered at $\delta = 1.0$ ppm. Also, the peak due to the $-CH_2-$ group of the MMA unit is overlapped with the $-CH_2-CH-$ group of the NAP unit and present at the highest field of $\delta = 2.4$ to 1.5 ppm. Figure 2 shows the ^{1}H-NMR spectrum for an NAP-MMA copolymer.

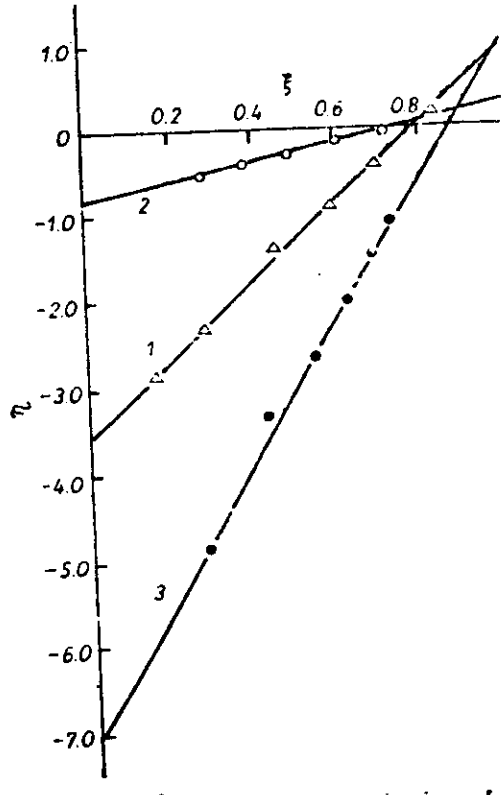


Fig. 4. KELEN-TÜDÖS plots for copolymerizations of NAP with (*1*) MA, (*2*) MMA, and (*3*) AN.

$$\xi = \frac{a^2}{ab + a^2} \quad \text{and} \quad \eta = \frac{a(b-1)}{ab + a^2}$$

where a and b are the molar ratios (M_1/M_2) of the comonomer in the feed and copolymer, respectively, and

$$\alpha = \frac{a_{min} \cdot a_{max}}{(b_{min} \cdot b_{max})^{1/2}}$$

Table 2. Monomer reactivity ratios for copolymerizations of NAP with MA, MMA and AN

M_1-M_2	FINEMAN-ROSS		KELEN-TÜDÖS		
	r_1	r_2	r_1	r_2	α
NAP-MA	0.922 ± 0.038	1.146 ± 0.067	0.961 ± 0.026	1.164 ± 0.023	0.325
NAP-MMA	0.292 ± 0.006	1.799 ± 0.019	0.297 ± 0.008	1.811 ± 0.033	2.221
NAP-AN	1.124 ± 0.056	1.336 ± 0.018	1.051 ± 0.026	1.289 ± 0.021	0.186

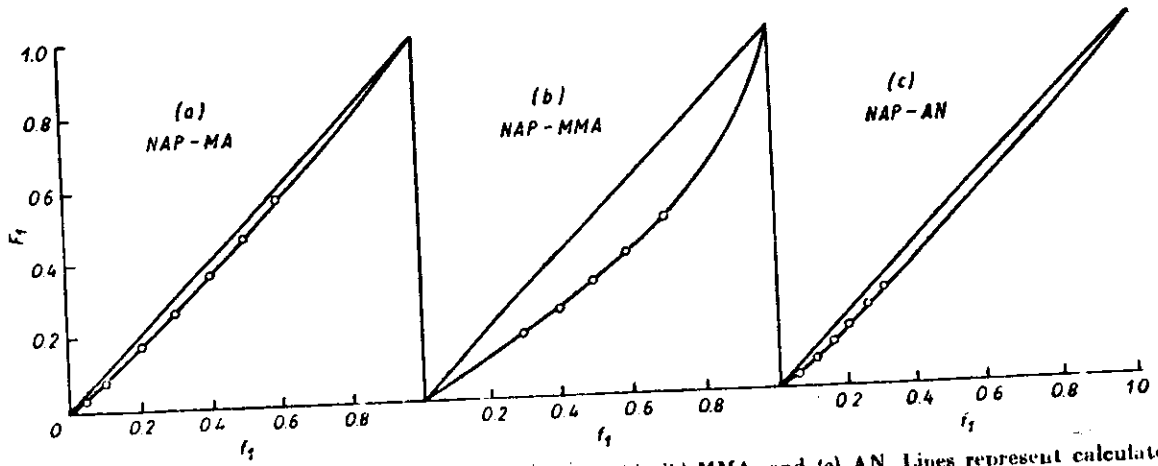


Fig. 5. Composition curves for copolymerizations of NAP with (a) MA, (b) MMA, and (c) AN. Lines represent calculated values and (∘) represent experimental values. f_1 — molar fraction of M_1 in feed and F_1 — molar fraction of M_1 in copolymer

The ^{1}H-NMR spectra of NAP-AN copolymer samples show the following characteristic peaks:

(i) One peak at $\delta = 7.9$ ppm due to the phenyl protons of the NAP units;

(ii) one peak centered at $\delta = 3.15$ ppm due to the methine protons of the AN units;

(iii) one peak centered at $\delta = 2.1$ ppm due to the methylene protons of the AN units and to the $-CH_2-\underset{|}{CH}-$ protons of the NAP units.

Figure 3 shows a typical spectrum of an NAP-AN copolymer sample as well as of polyacrylonitrile for comparison.

The approach of GRASSIE et al. [8] has been used to estimate the copolymer composition of each sample. From the copolymer structure the following expressions can be derived:

$I_{C_6H_4} \sim 4$ · (number of NAP units in the chain)

$I_{OCH_3} \sim 3$ · (number of MA or MMA units in the chain)

$I_{CH} \sim 1$ · (number of AN units in the chain)

where $I_{C_6H_4}$, I_{OCH_3}, and I_{CH} are the integrated peaks of the $-C_6H_4-$, $-OCH_3$ and $-CH-$ protons, respectively. If b is the molar ratio of M_1 and M_2 in the copolymer, then

$$I_{C_6H_4}/I_{OCH_3} = 4/3b \tag{1}$$

for NAP-MA or NAP-MMA copolymers and

$$I_{C_6H_4}/I_{CH} = 4b \tag{2}$$

for NAP-AN copolymer. Table 1 illustrates the analytical data for the copolymerization reaction of NAP with MA as an example.

From the values of feed and copolymer compositions, the monomer reactivity ratios were evaluated using the FINEMAN-ROSS [9] and KELEN-TÜDÖS [10] methods. Figure 4 shows the KELEN-TÜDÖS plots for the three studied systems. The values of r_1 and r_2 from the KELEN-TÜDÖS method are almost identical to those obtained by the FINEMAN-ROSS method. Typical values obtained by the two methods are tabulated in Table 2. The r_1r_2 value for NAP-MMA (0.54) indicates that the copolymer should have a random distribution of the monomer units, while for the NAP-MA and NAP-AN systems the r_1r_2 values (1.12 and 1.34, respectively) illustrate a low tendency of the monomers to laternate, and the copolymer should be composed mainly of small sequences of monomeric units of the same type. The composition curves of the three binary copolymerization reactions studied are illustrated in Figure 5, which indicates that all studied systems gave no azeotropic copolymers.

The Q and e values for NAP were calculated by using the ALFREY-PRICE equations [11]:

$$e_1 = e_2 \pm (-\ln r_1r_2)^{1/2} \tag{3}$$

$$Q_1 = (Q_2/r_2) \exp[-e_2(e_2 - e_1)] \tag{4}$$

The average Q and e values for NAP were obtained by using the monomer reactivity ratios determined in the present work as well as the literature values [12] of Q and e for the MA, MMA and AN. The product r_1r_2 for the NAP-MA and NAP-AN systems was found to be > 1 and was thus set equal to 1 so that equation (3) could be solved. The average Q and e values for NAP were found to be $Q = 0.48$ and $e = 1.02$, which is in agreement with those reported in the literature [12] for esters of acrylic acid.

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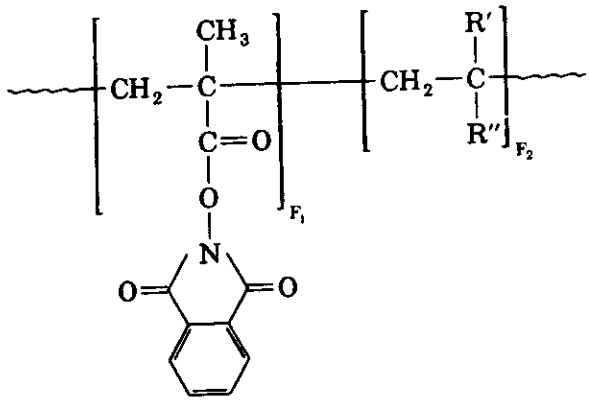
center cuts retained for use. Azobisisobutyronitrile (AIBN) was purified by recrystallization from absolute alcohol (m.p. 102°C).

The copolymers were obtained by solution polymerization. Predetermined amounts of the comonomers were placed in glass tubes, and diluted with dimethylformamide so that the total monomer composition was about 1.5 mol/L. Polymerization was commenced by adding AIBN in a concentration of 1 mol/100 mol monomers. The tubes were flushed with oxygen-free nitrogen for 10 min, capped, and thermostatted at 60°C for 30–60 min depending on the comonomer pairs and composition. The conversions were kept low (7–10%) and all copolymers were purified by reprecipitation from methanol, washed several times, dried, and weighed.

^{1}H NMR spectra of all the copolymer samples (in DMSO-d6 as a solvent and using TMS as zero reference), were obtained with a Varian EM-390 Spectrometer operating at 90 MHz.

RESULTS AND DISCUSSION

In the present investigation, the copolymerization parameters for NMP-MA, NMP-MMA, and NMP-AN systems were studied. The copolymer composition of each sample was calculated from ^{1}H NMR spectroscopy. The structure of the copolymer systems can be written as:



	R′	R″
NMP-MA	H	$COOCH_3$
NMP-MMA	CH_3	$COOCH_3$
NMP-AN	H	$C\equiv N$

The ^{1}H NMR spectra of NMP-MA copolymer samples showed the following characteristic peaks: (i) one peak at δ7.8 due to the phenyl protons of NMP units.[10] (ii) one peak at δ3.6 due to the methoxy protons of MA unit. (iii) one broad peak in the highest field centered at δ1.5 due to the α-methyl, methyne, and methylene protons of both NMP and MA units. Figure 1 shows typical spectrum for NMP-MA copolymer sample as an example.

The ^{1}H NMR spectra of NMP-MMA copolymer samples have the similar characteristic peaks except that the highest peak due to the α-methyl and methylene protons of both NMP and MMA units was centered at δ1.2. Figure

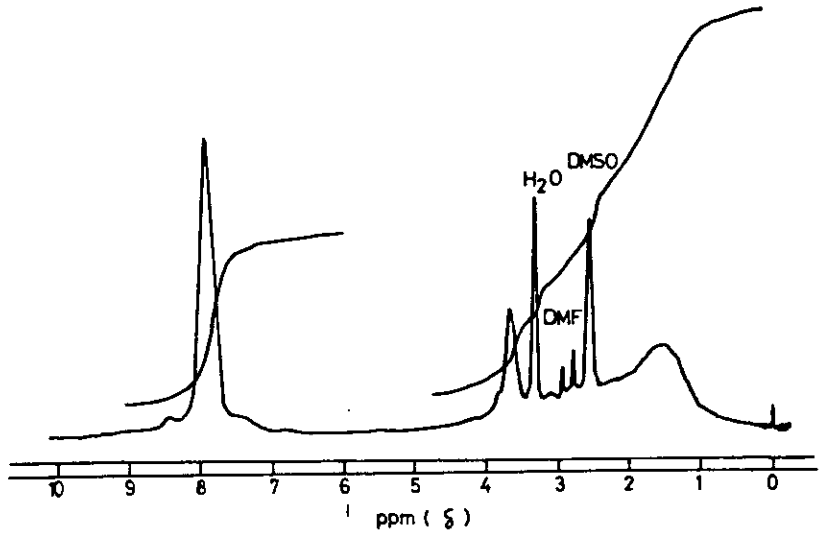


Fig. 1. ^1H NMR spectrum of NMP-MA copolymer sample prepared at molar fraction $f_1 = 0.40$.

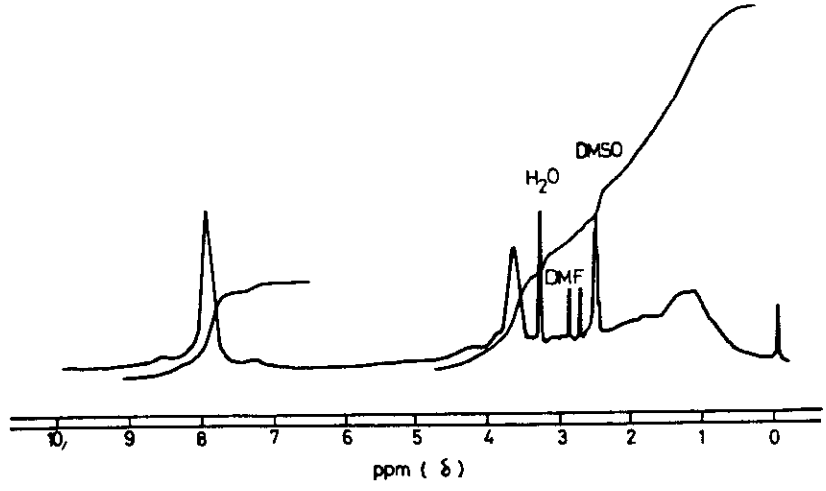


Fig. 2. ^1H NMR spectrum of NMP-MMA copolymer sample prepared at molar fraction $f_1 = 0.30$.

2 illustrates the ^1H NMR spectrum for a copolymer sample of NMP-MMA, as an example.

The ^1H NMR spectra of NMP-AN copolymer samples illustrates the following characteristic peaks:

1. One peak at $\delta 7.9$ due to the phenyl protons of NMP units.
2. One peak centered at $\delta 3.2$ due to methyne proton of AN units.
3. One peak centered at $\delta 2.2$ due to methylene protons of both NMP and AN units.
4. One peak at $\delta 1.65$ due to α-methyl protons of NMP units. Figure 3 shows typical spectrum for a sample of copolymer NMP-AN as example, as well as a sample of poly(acrylonitrile).

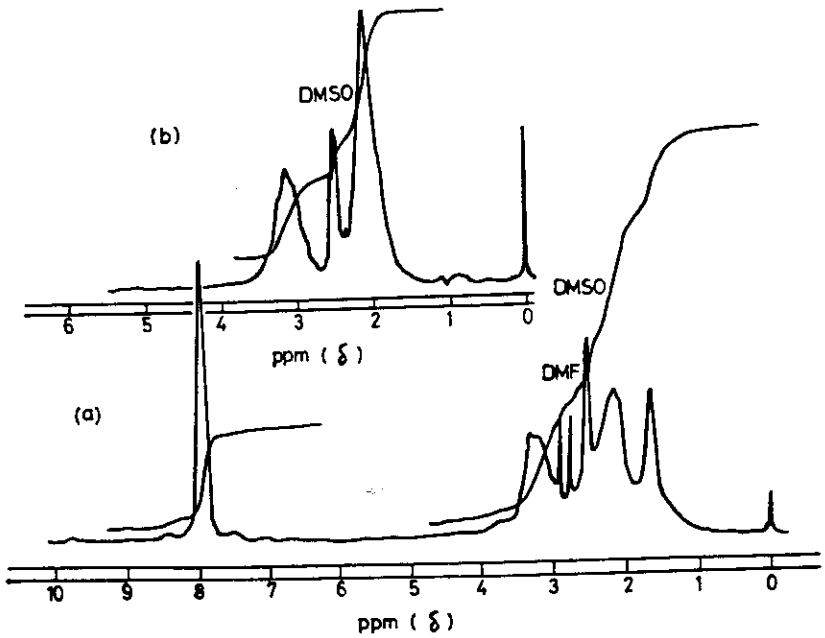


Fig. 3. ^{1}H NMR spectra of (a) NMP-AN copolymer sample prepared at molar fraction $f_1 = 0.10$ and (b) polyacrylonitrile.

The approach of Grassie et al.[16] has been used to estimate the copolymer composition of each sample. From the copolymer structure, the following expressions are derived:

$$I_{C_6H_4} \propto 4(\text{No. NMP units in chain})$$

$$I_{OCH_3} \propto 3(\text{No. MA or MMA units in chain})$$

$$I_{CH} \propto (\text{No. AN units in chain})$$

in which $I_{C_6H_4}$, I_{OCH_3}, and I_{CH} are the integrated tracers of $\diagdown C_6H_4$, $-OCH_3$ and $\diagdown CH-$ protons, respectively. If b is the molar ratio (M_1/M_2) in the copolymer, then:

$$I_{C_6H_4}/I_{OCH_3} = 4/3b \tag{1}$$

for NMP-MA or NMP-MMA copolymers and

$$I_{C_6H_4}/I_{CH} = 4b \tag{2}$$

for NMP-AN copolymer.

Tables I to III give the analytical data for copolymerization reactions of NMP with MA, MMA, and AN. From the values of feed and copolymer compositions, the monomer reactivity ratios were evaluated using the Fineman-Ross[17] and Kelen-Tüdős[18] methods. Figure 4 shows the Kelen-Tüdős

TABLE I
Analytical Data for Copolymerization of NMP with MA

Feed composition (a)	% Conversion	Copolymer composition (b)
2.3333	9.7	3.3750
1.5000	8.4	2.4827
1.0000	7.9	1.9883
0.6667	8.8	1.4353
0.4286	7.1	0.9681
0.2500	7.0	0.7045

*a and b are the molar ratios of M_1 and M_2 in the feed and copolymer, respectively.

TABLE II
Analytical Data for Copolymerization of NMP with MMA

Feed composition (a)	% Conversion	Copolymer composition (b)
2.3333	7.4	3.4351
1.5000	6.5	2.1464
1.0000	6.3	1.4000
0.6667	8.2	0.9138
0.4282	7.6	0.6389

TABLE III
Analytical Data for Copolymerization of NMP with AN

Feed composition (a)	% Conversion	Copolymer composition (b)
0.4286	8.3	1.0522
0.3333	8.5	0.8616
0.2500	6.8	0.7665
0.1765	7.5	0.5157
0.1111	8.3	0.4227
0.0526	7.1	0.1899

plots for the three systems studied. The values of r_1 and r_2 from the Kelen-Tüdős method are almost identical to those obtained by the Fineman-Ross method. Typical values obtained by the two methods are tabulated in Table IV. The r_1r_2 values for NMP-MA and NMP-AN systems (0.254 and 0.341, respectively) indicate that the copolymers in both cases should have a random distribution of the monomer units with a tendency toward alternation, while for the NMP-MMA system the r_1r_2 value (1.014) illustrates a low tendency of the monomer units to alternate and the copolymer should be composed mainly of small sequences of the same type. Figure 5 illustrates the composition curves and indicates that all systems studied gave no azeotropic copolymers.

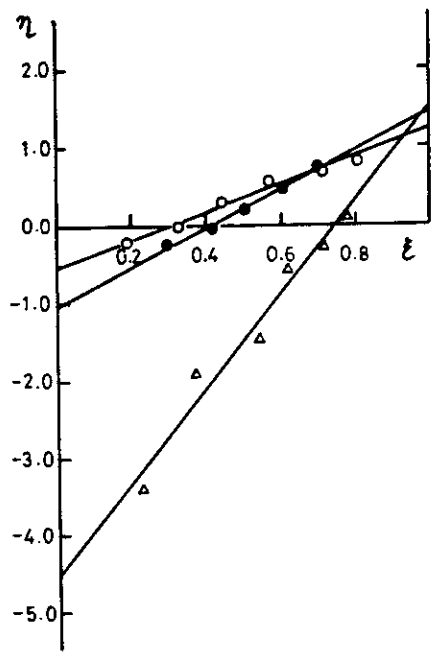


Fig. 4. Kelen-Tüdős plots for copolymerizations of NMP with (○) MA, (●) MMA, and (△) AN.

$$\xi = \frac{a^2}{ab + a^2} \quad \text{and} \quad \eta = \frac{a(b-1)}{ab + a^2}$$

where a and b are the molar ratios (M_1/M_2) of the comonomer in the feed and copolymer, respectively, and

$$\alpha = \frac{a_{\min} \cdot a_{\max}}{(b_{\min} \cdot b_{\max})^{1/2}}$$

TABLE IV
Monomer Reactivity Ratios for Copolymerizations of NMP with MA, MMA, and AN

	Fineman-Ross method		Kelen-Tüdős method		
$M_1 - M_2$	r_1	r_2	r_1	r_2	$r_1 r_2$
NMP-MA	1.147 ± 0.049	0.170 ± 0.039	1.223 ± 0.097	0.208 ± 0.029	0.254
NMP-MMA	1.370 ± 0.254	0.641 ± 0.239	1.441 ± 0.179	0.704 ± 0.110	1.014
NMP-AN	1.400 ± 0.211	0.223 ± 0.021	1.496 ± 0.162	0.228 ± 0.019	0.341

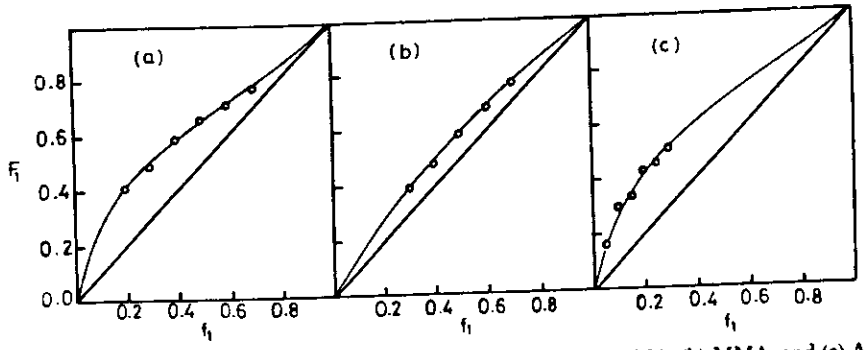


Fig. 5. Composition curves for copolymerizations of NMP with (a) MA, (b) MMA, and (c) AN. Line represents calculated values and (○) represent experimental values. f_1 = molar fraction of M_1 in feed and F_1 = molar fraction of M_1 in copolymer.

The Q and e values were calculated by using the Alfrey-Price equations[19]:

$$e_1 = e_2 \pm (-\ln r_1 r_2)^{1/2} \tag{3}$$

$$Q_1 = (Q_2/r_2)\exp[-e_2(e_2 - e_1)] \tag{4}$$

The Q and e values that represent the extent of resonance stabilization and polarity of the double bond, respectively, in a monomer and its radical are extensively tabulated by Young[20] from earlier copolymerization data. Thus, the Q and e values for NMP were obtained by using the monomer reactivity ratios determined for the copolymer systems NMP-MA, NMP-MMA, and NMP-AN (Table IV) and using the Q and e values for the MA, MMA, and AN.[20] The product $r_1 r_2$ value for NMP-MMA system was found to be > 1 and was thus set equal to 1 so that Eq. (3) could be solved.[21] The average Q and e values for NMP monomer were calculated and were found to be $Q = 0.90$ and $e = 0.01$, respectively, and are in agreement with those reported in the literature[20] for the esters of acrylic acid.

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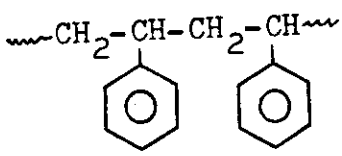
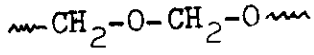
CHAPTER (I)

INTRODUCTION

The rapid increase in the range of manufactured products resulted directly from the development of a broad range of new fibres, plastics, elastomers, adhesives and resins. These new materials are polymers and their impart on our present way of life is almost incalculable. In 1920 Staudinger[1] published the key paper in the development of the modern view of polymer structure and specifically proposed chain formulas for polystyrene and polyoxymethylene.

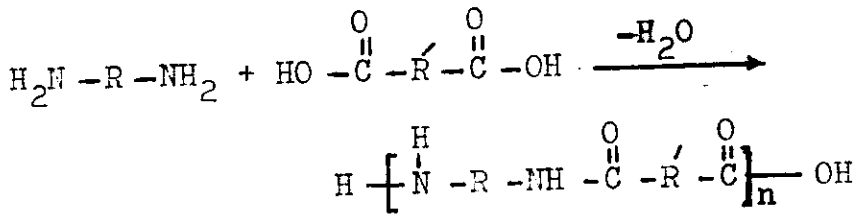


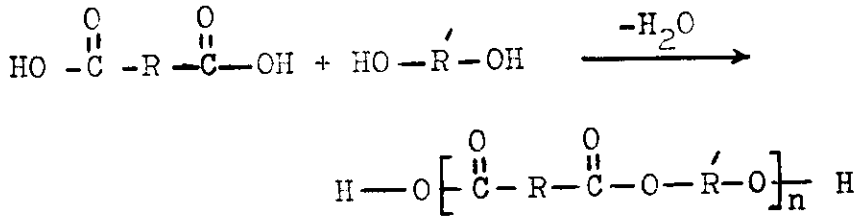


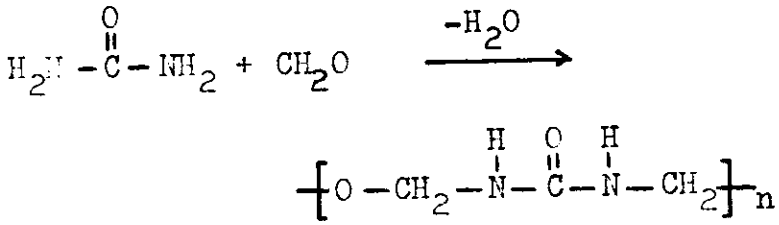
Carothers[2] demonstrated that condensation reactions could be used to form high polymers. He also established several important principles that underlie synthetic polymer chemistry to this day: (1) that monomers must be at least bifunctional; (2) that monomers must be relatively pure; and (3) that reactions used must be such as to proceed in nearly 100 % yield.

Polymers are classified according to the types of reactions involved in their synthesis. The three main polymerization reaction types are: (1) condensation

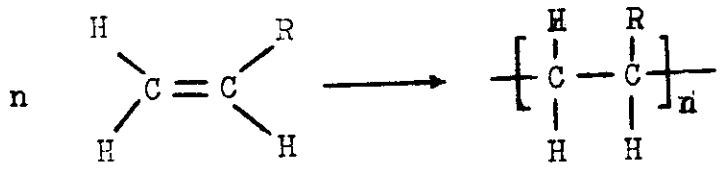
reactions, (2) addition reactions, and (3) ring opening polymerizations. Polymerization by condensation is used as a basis for the manufacture of many important polymers, such as nylon, polyesters, phenol-formaldehyde, and urea-formaldehyde resins, as follows:





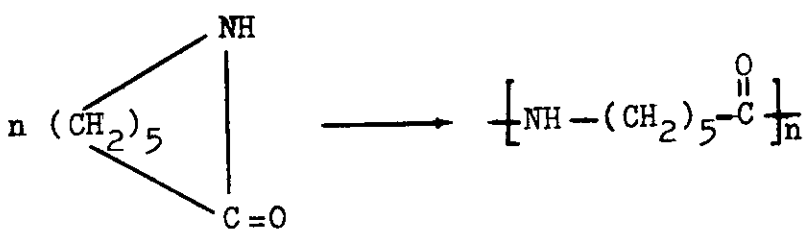


Addition polymers are macromolecules formed by the addition reactions of olefins, acetylenes, aldehydes, or other compounds with unsaturated bonds,



Many well-known thermoplastics are addition-type polymers, the differences between the various materials being mainly connected with the presence of different substituent groups attached to the main chain.

The treatment of some cyclic compounds with catalysts brings about cleavage of the ring followed by polymerization to yield high-molecular weight polymers.



Free-Radical Addition Polymerization:

In a free-radical addition polymerization, the growing chain end bears an unpaired electron. Addition of each monomer molecule to the chain end involves an attack by the radical site on the unsaturated monomer. Thus, the unpaired electron is transferred to the new chain end at each addition step. Free-radical polymerization reactions are of enormous importance in technology. The monomers for these reactions are available in large quantities from the petrochemical industry (e.g. from reaction sequences that start from ethylene, acetylene, or acetone), and the polymers obtained from these monomers form the foundation of much of the polymer industry.

Many common synthetic materials, such as polyethylene, polystyrene, and polymethyl methacrylate, are made by free-radical polymerization. All these polymerizations involve the same mechanistic sequence. First a free radical initiator adds to a monomer and produce a new free radical.

$$R^{\bullet} + CH_2{=}CHX \longrightarrow R\text{-}CH_2\text{-}\dot{C}H\text{-}X$$

The new radical starts a chain by adding to another monomer.

$$R\text{-}CH_2\text{-}\dot{C}HX + CH_2{=}CHX \longrightarrow$$

$$R\text{-}CH_2\text{-}CHX\text{-}CH_2\text{-}\dot{C}HX$$

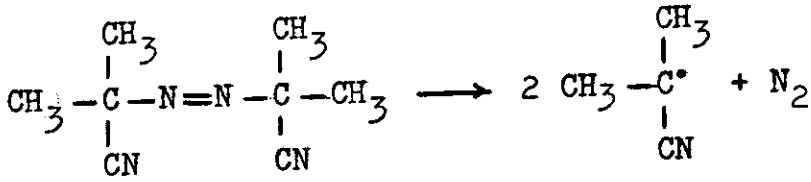
This step repeats, increasing the chain by one monomer unit at a time. The chain terminates by coupling with another free radical, or by disproportionation.

A free radical is usually obtained by homolysis of an ordinary covalent bond. Examples include peroxide dissociation, halogen photolysis, and azo compound decomposition:

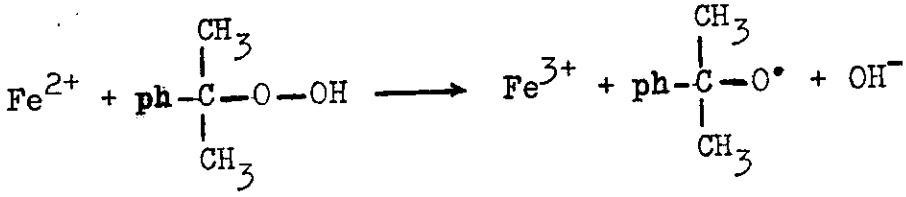
$$R\text{-}O\text{-}O\text{-}R \xrightarrow{\Delta} 2\ R\text{-}O^{\bullet}$$

$$Cl\text{-}Cl \xrightarrow{h\nu} 2\ Cl^{\bullet}$$

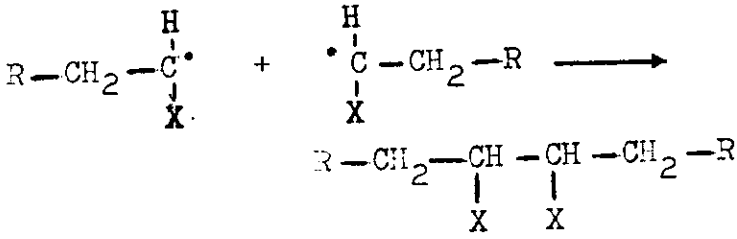
$$CH_3\text{-}N{=}N\text{-}CH_3 \longrightarrow 2\ H_3C^{\bullet} + N{\equiv}N$$

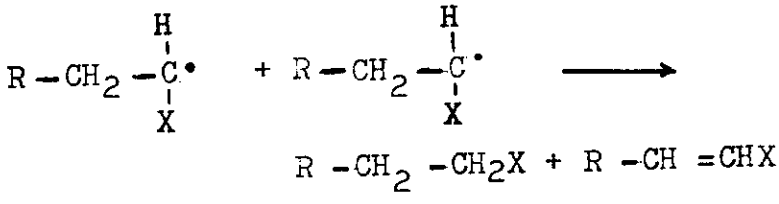


A free radical can also form in a one-electron oxidation-reduction reaction. Ferrous ion and cumene hydroperoxide produce oxy radicals even at $0^{\circ}C$.



Alkyl radicals, the type responsible for propagation can be destroyed in two ways, by combination and by disproportionation:





In the first case, the product contains two initiator units per molecule. In the second case, half the product molecules are terminal olefins.

Besides terminating by combination or disproportionation, a chain may abstract an atom from another molecule. This terminates the original chains growth, but it creates another free radical.

$$R-CH_2-\dot{C}H_2 + R-H \longrightarrow R-CH_2-CH_3 + R^{\bullet}$$

This reaction is called chain transfer and may occur with initiator, monomer, solvent, polymer, or an impurity. A material deliberately added to a system to control molecular weight by chain transfer is called chain-transfer agent. The new radical derived from the chain-transfer agent may initiate a new chain in the usual way.

$$R^{\bullet} + CH_2=\underset{X}{CH} \longrightarrow R-CH_2-\dot{\underset{X}{C}}H$$

Because the process does not decrease the concentration of radicals in the system, it does not affect the overall rate of polymerization. It does, however, reduce the molecular weight of the product.

Kinetics of Free-Radical Polymerization [3-6]

The overall rate of polymerization as well as the length of the polymeric chains formed in addition polymerization are determined by the rates of the individual processes of initiation, propagation, and termination.

The overall mechanism for the conversion of monomer to polymer by use of a typical free-radical initiator, I, can be described by the following set of rate equations :

$$I \xrightarrow{k_d} 2\,R^{\bullet}$$

initiation

$$R^{\bullet} + M \xrightarrow{k_i} R\text{-}M^{\bullet}$$

$$R\,M^{\bullet} + M \xrightarrow{k_p} R\sim MM^{\bullet}$$

propagation

$$R\sim M^{\bullet} \xrightarrow{k_t} R\sim M\text{-}M\sim R$$

termination

$$R\sim M^{\bullet} \xrightarrow{k_t} R\sim MH + R\sim M$$

By making several assumptions relatively simple expression for the rate of polymerization (R_p) may be obtained:

1- The rate of formation of free radical is equal to the rate of consumption of free radicals.

2- In the propagation step, radical activity is independent of chain length.

3- The rate of production of chain radicals is equal to the rate of termination of chain radical, i.e.

$r_i = r_t$ and $\left.\frac{d(M^{\bullet})}{dt}\right|_{overall} = 0$

4- The rate of polymerization is equall to the rate of propagation.

During termination reactions two chain radicals $R\sim M^{\bullet}$ combine to give a polymer molecule and the rate equation is:

$$r_t = \frac{-d(R\sim M^{\bullet})}{dt} = k_t(R\sim M^{\bullet})$$

at the steady state:

$$r_i = r_t = k_t(R\sim M^{\bullet})^2 = k_i I$$

Thus, $$\left[R\sim M^{\bullet}\right] = \sqrt{\frac{k_i}{k_t}\left[I\right]}$$

Hence, the rate of polymerization is equal to the rate of propagation, the rate equation becomes:

$$r_p = \frac{-d[M]}{dt} = k_p[M]\left[R\sim M^{\bullet}\right]$$

$$r_p = k_p[M]\sqrt{\frac{k_i}{k_t}[I]} = k_p[M]\left(\frac{k_i}{k_t}[I]\right)^{\frac{1}{2}}$$

The rate of polymerization equation predicts that the rate of formation of polymer should be proportional to the square root of the initiator concentration and the first power of the monomer concentration.

Copolymerization[7-9]

The simultaneous polymerization of two or more monomers is called copolymerization. A copolymer is thus defined as a polymer having at least two different monomers incorporated into one polymeric chain. Interest has been centered on copolymerization, because it is

often found that the copolymer has more desirable mechanical properties than the respective homopolymers. One may also introduce a comonomer into a polymer to render it receptive to dyes or provide sites for cross-linking the polymer chains. Many commercial polymers are copolymers.

Binary Copolymerization Reactions:

To be able to predict the composition of a copolymer before the polymerization is extremely useful. This can be accomplished by the copolymer composition equation. The four possible propagation steps in a copolymerization are the following:

	Growing Chain		Monomer Added			Rate
(i)	$\sim\sim m_1^{\bullet}$	+	M_1	$\xrightarrow{k_{11}}$	$\sim\sim m_1^{\bullet}$	$k_{11}[m_1^{\bullet}][M_1]$
(ii)	$\sim\sim m_1^{\bullet}$	+	M_2	$\xrightarrow{k_{12}}$	$\sim\sim m_2^{\bullet}$	$k_{12}[m_1^{\bullet}][M_2]$
(iii)	$\sim\sim m_2^{\bullet}$	+	M_1	$\xrightarrow{k_{21}}$	$\sim\sim m_1^{\bullet}$	$k_{21}[m_2^{\bullet}][M_1]$
(iv)	$\sim\sim m_2^{\bullet}$	+	M_2	$\xrightarrow{k_{22}}$	$\sim\sim m_2^{\bullet}$	$k_{22}[m_2^{\bullet}][M_2]$

where M_1 and M_2 are monomer one and two, respectively, $m_1^{\bullet}$ denotes the polymer chain with a terminal monomer

one, and $m_2^\bullet$ is the polymer chain with a terminal monomer two, (i.e, there is no penultimate unit effect). The analysis is further simplified by a steady-state assumption: the rate of disappearance of a chain end equals the rate of its appearance. Therefore, the rate of reaction (ii) must equal the rate of reaction (iii):

$$k_{12}[m_1^\bullet][M_2] = k_{21}[m_2^\bullet][M_1]$$

$$\frac{[m_1^\bullet]}{[m_2^\bullet]} = \frac{k_{21}[M_1]}{k_{12}[M_2]}$$

The rates of disappearance of monomers one and two are:

$$\frac{-d[M_1]}{dt} = k_{11}[m_1^\bullet][M_1] + k_{21}[m_2^\bullet][M_1]$$

$$\frac{-d[M_2]}{dt} = k_{22}[m_2^\bullet][M_2] + k_{12}[m_1^\bullet][M_2]$$

After combining and rearranging, these equations, we obtain:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{(k_{11}/k_{12})[M_1] + [M_2]}{(k_{22}/k_{21})[M_2] + [M_1]}$$

We can now define the important quantities termed the monomer reactivity ratios (r_1 and r_2) as follows:

$$r_1 = \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_2 = \frac{k_{22}}{k_{21}}$$

Thus the copolymer composition equation can be obtained as:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}$$

Monomer Reactivity Ratios

If $r < 1$ the growing chain prefers to add the comonomer rather than its own kind, and if $r > 1$ the growing chain prefers to add its own kind rather than the other comonomer. There are a number of different combinations of reactivity ratio values that are of special interest:

(a) $r_1 > 1$ and $r_2 > 1$: In this case, two homopolymers would be formed.

(b) $r_1 r_2 = 1$: A copolymer that is described by the above reactivity ratios is termed an ideal copolymer, in which the monomers are randomely distributed throughout the chain. The amount of any monomer incorporated into a polymer chain is simply dependent on the concentration of that monomer on the feed and the relative reactivities of the two monomers.

(c) $r_1 = r_2 \neq 0$: An alternating copolymer results from a system having the above reactivity ratios. The copolymer has alternating units of the two monomers because each monomer reacts exclusively with the other monomer. There are many monomers, such as maleic anhydride, which do not homopolymerize except under special conditions but readily form copolymers.

Methods of Determination of Monomer Reactivity Ratios[10]

(i) Direct Curve Fitting

Reactivity ratios may be obtained from direct curve fitting of polymer-monomer composition curves. This is not a favored method, however, beacuse the composition curve is insensitive to small changes in the reactivity ratios.

(ii) Mayo and Lewis Method[11]

The most common method used is that of Mayo and Lewis. Rearranging the copolymer composition equation into the form of the equation for a straight line ($y = mx + b$) as follows:

$$r_2 = \left(\frac{[M_1]}{[M_2]}\right)^2 \frac{[m_2]}{[m_1]} r_1 + \frac{[M_1][m_2]}{[M_2][m_1]} - 1$$

Every set of M_1, M_2 and m_1, m_2 values produces a straight line. By setting r_1 equal to arbitrary values, corresponding values of r_2 can be found and a straight line drawn for a specific set of M_1, M_2 and m_1, m_2 values. The propaple values of r_1 and r_2 lie in the area cut out by the intersecting lines.

(iii) Fineman-Ross method[12]

Fineman and Ross were the first who arrange the

differential copolymer composition equation in the following form:

$$a - \frac{a}{b} = r_1 \frac{a^2}{b} - r_2$$

where $a = \frac{[M_1]}{[M_2]}$, the molar ratio of monomer feed, and

$b = \frac{m_1}{m_2}$, the molar ratio of the copolymer.

By plotting $a - a/b$ as the ordinate aganist a^2/b as abcissa, the slope of the straight line is r_1 and the intercept is $-r_2$. When the polymer composition measurements are precise, this method is very convenient and frequently used due to its simplicity and accuracy.

(iv) Joshi-Kapur method[13]

This method eleminates the subjective error in the location of the best point in the intersection method of Mayo-Lewis plot.

(v) Tidwell-Mortimer method[14]

In detalied critical treatises, Tidwell and Mortimer pointed out the defects of the different methods, and suggested a standared computerized procedure; the nonlinear least square method. This method presumes that there is no possible experimental error in the independent variable; the monomer composition of the feed; and that

the absolute error in the copolymer composition is independent of its value or constant.

(vi) Yezrielev-Brokhina-Roskin method[15]

Yezrielev, Brokhina and Roskin transformed the linear equation of copolymer composition into the symmetrical form as:

$$a/b^{\frac{1}{2}}.r_1 - b^{\frac{1}{2}}/a.r_2 + (1/b^{\frac{1}{2}} - b^{\frac{1}{2}}) = 0$$

where $a = M_1/M_2$ (molar ratio of the two monomers in the comonomer mixture).

and $b = m_1/m_2$ (molar ratio of the two monomers in the copolymer).

In this method the theoretical line is situated evenly between the experimental points of positive and negative error which leads to determination of reactivity ratios more accurate.

(vii) Kelen-Tudos method[16]

Kelen and Tudos published a method for calculating the monomer reactivity ratios based on a new graphically evaluable linear equation as follows:

$$\eta = (r_1 + \frac{r_2}{\alpha})\xi - \frac{r_2}{\alpha}$$

where:

$$\eta = \frac{a(b-1)}{\alpha b + a^2} \quad , \quad \xi = \frac{a^2}{\alpha b + a^2} \quad \text{and}$$

$$\alpha = \frac{a_{min.} \times a_{max.}}{\sqrt{b_{min.} \times b_{max.}}}$$

The variable ξ cannot take any positive value, only those in interval of ξ 0-1. Thus, plotting the η values as the function of $\xi = 0$ to $\xi = 1$ gives $-r_2/\alpha$ and r_1, respectively (both as intercepts).

Factors affecting monomer reactivity ratios

With respect to free-radical copolymerization, it may be stated that reactivity ratios are comparatively little influenced by most common variables such as conversion, solvent and method of polymerization[17]. In the range of temperatures from room temperature to about 100°C there is little variation in reactivity ratios in binary copolymerizations. However, there is a tendency for the $r_1 r_2$ product to approach 1 as temperature increases. Copolymerization has been affected at temperature as −78°C and temperature as high as 130°C, with large change in reactivity ratios. With respect to the solvent, numerous studies have been made which indicate that a change of solvent has little effect on monomer reactivity ratios. Accordingly, a highly polar or nonpolar solvent, does not appear to influence the value of reactivity ratios. The effects of dilution on reactivity ratios have been studied and it has been concluded that no

substantial effect exists. Also, polymerization by solvent-nonsolvent techniques gives reactivity ratios similar to those of homogeneous system, that is the precipitation of copolymers during polymerization does not alter reactivity ratios. Monomer reactivity ratios have also been found to vary with pressure, for example, copolymerization of methyl methacrylate and acrylonitrile,[18] the product of $r_1 r_2$ increased from 0.16 (at atmospheric pressure) to 0.91 (at 1000 atmosphere) indicating that increased pressure increases the tendency for this system towards blocks.

Individual Monomer Reactivity in Copolymerization :

In a copolymerization reaction the reactive end of the growing chain is a free radical derived from one of the two monomers. Obviously, two types of reactive ends can excist and for this reason, reactivity ratios must be determined in pairs. Moreover because the values obtained experimentally are relative values, the reactivity ratios must be determined experimentally for each pair of monomers. A correlation procedure that permits the assignment to each monomer of a reactivity parameter that is applicable to its copolymerization with all other monomers would represent a great economy in data accumulation and tabulation. One approach to developing such correlation takes into account the resonance and polar

factors inherent in the monomers and is called the Alfrey-Price Q—e relationship.[19] Q is a measure of the resonance stability of a monomer in copolymerization, and e is a polar factor. The fundamental equations are given as :

$$r_1 = (k_{11}/k_{12}) = \left[Q_1/Q_2\right] \exp. \; - e_1(e_1 - e_2)$$

$$r_2 = (k_{22}/k_{21}) = \left[Q_2/Q_1\right] \exp. \; - e_2(e_2 - e_1)$$

$$r_1 r_2 = \exp. \left[- (e_1 - e_2)^2\right]$$

$$\ln r_1 r_2 = - (e_1 - e_2)^2$$

Price chose styrene as the standard monomer with the values Q = 1 and e = -0.8. The Q and e values of any monomer that has been copolymerized with styrene can be calculated from the r_1 and r_2 values given in literature. Conversely, knowing the Q and e for any two monomers, the r_1 and r_2 values can be calculated for this monomer pair, whether or not they have ever been copolymerized. While the predicted behaviour is not always exactly like the experimental result, the Alfrey-Price Q—e scheme nevertheless leads at least to a good approximations. The major shortcoming of the Q—e scheme is that all radical polymerizations involve not only resonance and polar factors, but also steric factors. It is certainly conceded that steric factors limit the applicability of the scheme which is considered as an empirical

method of correlation.

Terpolymer composition equation

Chemists sometimes polymerize mixture of three (or more) monomers with the intent of preparing multicomponent polymers that will have the properties required for a specific use. The commercial importance of multicomponent polymerization has rapidly increased in the last decade. Incorporation of a third monomer developed gross effects on the properties of copolymers such as heat resistance, tensile strength, elasticity, transparency and solvent resistance. It is desirable to know the relationship between the ratio of a given set of monomers and the corresponding copolymer composition. It has been shown by Alfrey and Goldfinger[20] that there are nine propagation reactions in the determination of terpolymer composition.

$$\sim M_1^{\bullet} + M_1 \xrightarrow{k_{11}} \sim M_1 - M_1^{\bullet} \qquad \sim M_2^{\bullet} + M_1 \xrightarrow{k_{21}} \sim M_2 - M_1^{\bullet} \qquad \sim M_3^{\bullet} + M_1 \xrightarrow{k_{31}} \sim M_3 - M_1^{\bullet}$$

$$\sim M_1^{\bullet} + M_2 \xrightarrow{k_{12}} \sim M_1 - M_2^{\bullet} \qquad \sim M_2^{\bullet} + M_2 \xrightarrow{k_{22}} \sim M_2 - M_2^{\bullet} \qquad \sim M_3^{\bullet} + M_2 \xrightarrow{k_{32}} \sim M_3 - M_2^{\bullet}$$

$$\sim M_1^{\bullet} + M_3 \xrightarrow{k_{13}} \sim M_1 - M_3^{\bullet} \qquad \sim M_2^{\bullet} + M_3 \xrightarrow{k_{23}} \sim M_2 - M_3^{\bullet} \qquad \sim M_3^{\bullet} + M_3 \xrightarrow{k_{33}} \sim M_3 - M_3^{\bullet}$$

In order to predict the behaviour of a three component system ($M_1 - M_2 - M_3$), it is necessary to know the copolymerization parameters of the three separated two-component copolymerizations as follows :

$M_1 - M_2$	$M_2 - M_3$	$M_1 - M_3$
$r_1 = k_{11}/k_{12} = r_{12}$	$r_1 = k_{22}/k_{23} = r_{23}$	$r_1 = k_{11}/k_{13} = r_{13}$
$r_2 = k_{22}/k_{21} = r_{21}$	$r_2 = k_{33}/k_{32} = r_{32}$	$r_2 = k_{33}/k_{31} = r_{31}$

In a manner completely analogous to that described for the two component systems (page 9) the terpolymerization composition equation, which relates the instantaneous terpolymer composition to the feed of monomers (using the assumption of steady state), could be obtained as :

$$d[M_1] : d[M_2] : d[M_3] = M_1\left[\frac{[M_1]}{r_{31}r_{21}} + \frac{[M_2]}{r_{21}r_{32}} + \frac{[M_3]}{r_{31}r_{23}}\right]\left[[M_1] + \frac{[M_2]}{r_{12}} + \frac{[M_3]}{r_{13}}\right]$$

$$: M_2\left[\frac{[M_1]}{r_{12}r_{31}} + \frac{[M_2]}{r_{12}r_{32}} + \frac{[M_3]}{r_{32}r_{13}}\right]\left[[M_2] + \frac{[M_1]}{r_{21}} + \frac{[M_3]}{r_{23}}\right]$$

$$: M_3\left[\frac{[M_1]}{r_{13}r_{21}} + \frac{[M_2]}{r_{23}r_{12}} + \frac{[M_3]}{r_{13}r_{23}}\right]\left[[M_3] + \frac{[M_1]}{r_{31}} + \frac{[M_2]}{r_{32}}\right]$$

Terpolymerization composition equation has been tested by a number of workers and has been found to describe experimental copolymerization within the limits to be expected from the accuracy of the reactivity values[21-23].

Ham[24] proposed a simpler expression for the terpolymer composition equation when polar and steric effects

are absent or when polar effects between the various radicals and monomers are similar so that :

$$r_{12}\, r_{23}\, r_{31} = r_{13}\, r_{32}\, r_{21}$$

and the terpolymer composition equation was simplified in the form :

$$d[M_1] : d[M_2] : d[M_3] = M_1 \left[M_1 + \frac{M_2}{r_{12}} + \frac{M_3}{r_{13}} \right] :$$

$$M_2 \frac{r_{21}}{r_{12}} \left[\frac{M_1}{r_{21}} + M_2 + \frac{M_3}{r_{23}} \right] :$$

$$M_3 \frac{r_{31}}{r_{13}} \left[\frac{M_1}{r_{31}} + \frac{M_2}{r_{32}} + M_3 \right]$$

Mayo[25] reported that Ham's equation is potentially useful for bringing out inconsistencies between experimental data are theoretical correlations and prediction of behaviours of monomers in copolymerizations. Also, Ham's probabilities are sometimes quite good and sometimes very poor.

Khan and Horowitz[26] studied the terpolymerization of vinyl acetate-dioctyl fumarate-N-vinyl pyrrolidone system and programmed the differential terpolymer composition equation on a digital computer in the following form :

$$dM_1 : dM_2 : dM_3 =$$

$$M_1\left[M_1 r_{23} r_{32} + M_2 r_{31} r_{23} + M_3 r_{32} r_{21}\right]\left[M_1 r_{12} r_{13} + M_2 r_{13} + M_3 r_{12}\right] :$$

$$M_2\left[M_1 r_{32} r_{13} + M_2 r_{13} r_{31} + M_3 r_{12} r_{31}\right]\left[M_2 r_{21} r_{23} + M_1 r_{23} + M_3 r_{21}\right] :$$

$$M_3\left[M_1 r_{12} r_{23} + M_2 r_{13} r_{21} + M_3 r_{12} r_{21}\right]\left[M_3 r_{31} r_{32} + M_1 r_{32} + M_2 r_{31}\right]$$

LITERATURE REVIEW

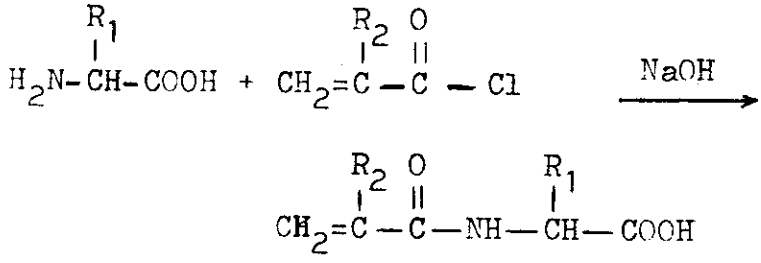
Multifunctional Polymers

The last years have seen the rise in popularity of the idea of attaching chemically reactive species to insoluble supports. Applications have been found in organic chemistry, inorganic chemistry, biochemistry, and biology. With polymeric resins, the question of whether to modify a preformed support chemically or to carry out a suspension copolymerization employing an appropriately functionalized comonomer is usually settled by the relative difficulty of the latter technique, and the ready availability of non-functionalized supports of very high quality. Nevertheless, copolymerization techniques do have a number of advantages. Generally the degree of functionalization of the product is more readily controlled, and the structure of the required group can be ascertained unambiguously by analysis of the relevant comonomer prior to polymerization. In addition, it is possible to predict to some extent the distribution of groups within the support.

The introduction of a functional group during polymerization requires first of all an appropriately substituted monomer to be made available. A wide variety of vinyl-derivatized molecule can be obtained from commercial sources and be polymerized or copolymerized to produce an appropriately functionalized support.

The synthesis of multifunctional polymers by preparation and polymerization or copolymerization of the correspoding monomers, however, may be difficult or even impossible if complex structures are required, or if the desired functions are able to interfere in the polymerization processes. A convenient indirect route to multifunctional polymers is to synthesize first macromolecules with chemical functions able to selectively and quantitatively react with hydroxyl or amino groups, giving ester or amidic bonds. By a subsequent reaction step with alcohols or amines bearing the desired groups attached as substituents, multifunctional polymers may be obtained.

Iwakura et al.[27] reported that the acylation of α-amino acids with acryloyl- or methacryloyl chloride gave the corresponding acrylamide as methacrylamide derivatives, respectively.

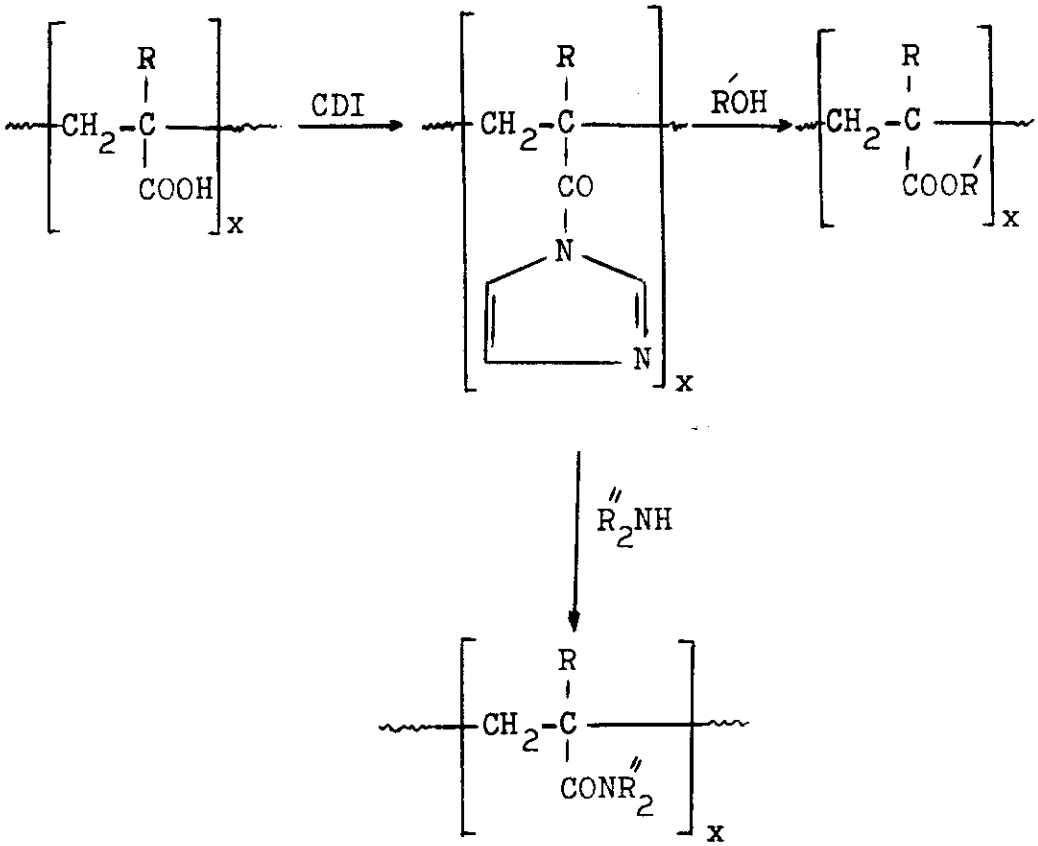


Rozyakhuno et al.[28] reported that cellulose acetate methacrylate and cellulose acetate sorbate were prepared by treatment of cellulose in CH_2Cl_2 containing a H_2SO_4

catalyst with mixtures of Ac_2O and methacrylic or sorbic acid that had been boiled 5 min.. The introduction of methacrylate or sorbate ester groups into the cellulose acetate increases its flexibility and extensibility. Ethylene-vinyl acetate copolymer and methacrylates were ester-exchanged in the presence of monocarboxylic acid esters (as the viscosity-lowering agent), esp. Me acetate, beta-methoxyethyl acetate, and Me lactate to give graft-activated copolymer[29]. Thus, Everflex 460 (19 wt. % vinyl acetate) 180, toluene 1.275, Me acetate 15, and Me methacrylate 309 were stirred 2 hr at 70 deg., mixed with 35 m. moles excess BuOH soln. of NaOBu and reacted 2 hr to give an activated copolymer (0.206 m. mole/g methacrylic acid group). Batz et al.[30] studied the reactivity of cyclohexylamine and NH_3 with polymers prepared from reactive acrylates, methacrylates, or N-vinyl-carbamates of N-hydroxysuccinimide, 1-hydroxy-1H-benzotriazole, and 2,4,5-trichlorophenol (or the resp. copolymers with 1-vinylpyrrolidinone, methacrylamide, acrylamide, or styrene) and indicated that the polymers would react with pharmacologically active compounds without racemization or side reactions. Diels-Alder addition of trans-piperylene with $CH_2=CMeCO_2H$ or its Me ester was carried out at 20-260 degree and hydrogenated products were separated by gas-liquid chromatography[31]. The structural and steric orientation coeffs. were calculated and correlated with the energy and entropy of activation of

the formation of isomeric adducts. Polymers containing acyl-activated ester groups were prepared through the reaction of amino groups of oligomers containing end carboxyl groups with nitrated N-(4-hydroxyphenyl)succinimide polymers. Thus, 3 g N-(4-hydroxy-3-nitrophenyl) succinimide polymers (OH sim. 9.1 m equiv.) in 70 ml DMF was mixed with 282 g benzyloxycarbonyl-glycine, mixed 2 hr at 3 deg. with 2.8 g dicyclohexylcarbodiimide in 10 ml DMF, and kept 18 hr at room temperature, to give 3.76 g desired polymers[32].

Ferruti et al.[33] studied the preparation and polymerization of 1-acryloylbenzotriazole and reported that the resulting poly-1-acryloylbenzotriazole, gave pure polyacrylic esters and polyacrylamides by reaction under mild conditions with alcohols and amines. Ferruti and Cottica[34] studied the preparation and polymerization of N-acryloxysuccinimide, N-methacryloxysuccinimide, and 1-acryloylbenzotriazole, as well as the exchange ability of the resulting polymers with alcohols and amines. Also, Ferruti and Vaccaroni[35] reported that, pure N-methacryloylimidazole was easily prepared, but it did not polymerize well by radical or ionic initiators. They studied the reaction of poly(acrylic acid) and poly(methacrylic acid) with N,N-carbonyldiimidazole (CDI), and then treating the reaction mixture with alcohols or amines, as follows:

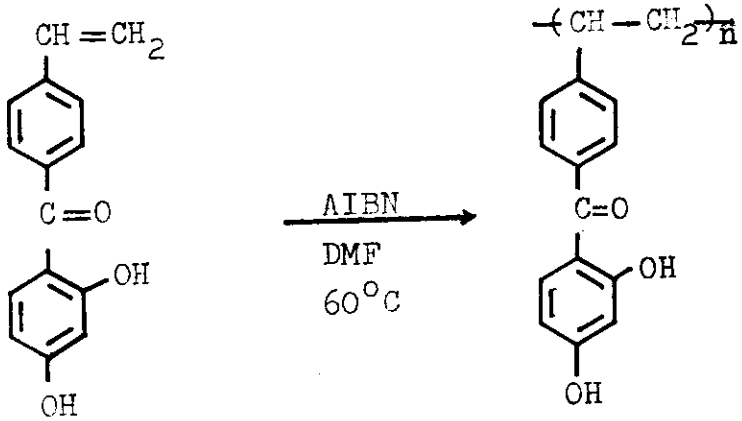


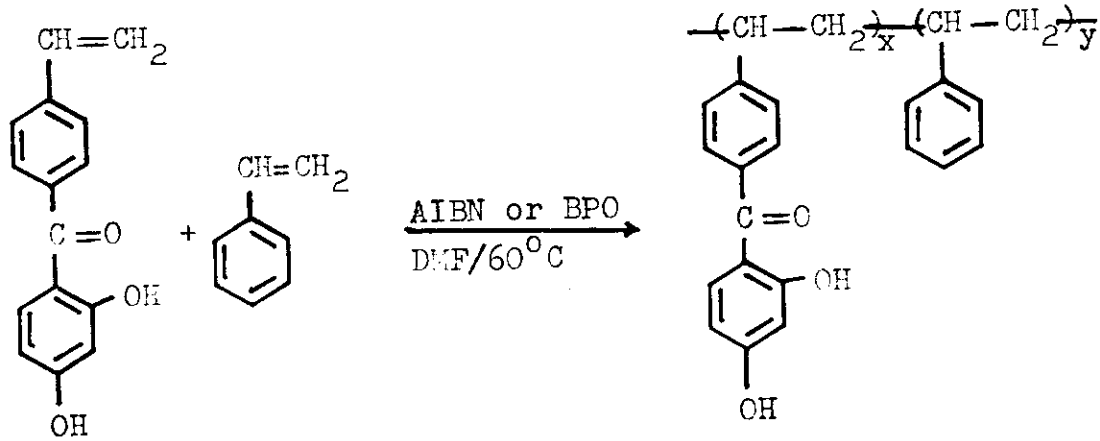
The reaction with poly(acrylic acid) was practically quantitative, only partial conversion occured in the case of poly(methacrylic acid). This may be due either to an incomplete formation of polyimidazole, or to an incomplete reaction of the polyimidazolide itself with alcohols or amines.

Koester and Heidmann[36] studied the polymerization of ethoxycarbonylmethyl acrylate 17.8, dimethylacrylamide 1.8, and N,N-ethylenebis(N-methylacrylamide) 0.49 in aq. soln. with azo-bis-isobutyronitrile for 2 hr each at 60, 70, and 80 degree to produce a reactive polymer. Reaction of the polymer with Me_2NH in Me_2CO-HOAc gave a crosslinked poly(dimethylacrylamide), which could not be obtained directly in pearl form because of the miscibility of dimethylacrylamide with most solvents. Partial hydrolysis of the latter polymer gave a substrate suitable for solid-phase synthesis of oligonucleotides. A styrene copolymer containing succinimide was prepared by treating styrene-maleic anhydride copolymer with $p\text{-}H_2NC_6H_4OH$ and nitrating[37]. This succinimide-containing copolymer was esterified with $phCH_2O_2C\text{-}X\text{-}OH$ (X=Gly, Leu, Gly-Gly, Leu-Leu) to give the corresponding active esters which were treated with cyclohexylamine, glycine Et ester, or leucine Et ester to give the appropriate cyclohexylamide or peptide Et ester. Esterification of N-(tert-butoxycarbonyl)prolylprolyl-β-alanine with $CF_3CO_2C_6H_4NO_2\text{-}p$ and trifluoroacetolysis of the ester gave p-nitrophenyl prolylprolyl-β-alanine av. yield 71 %[38].

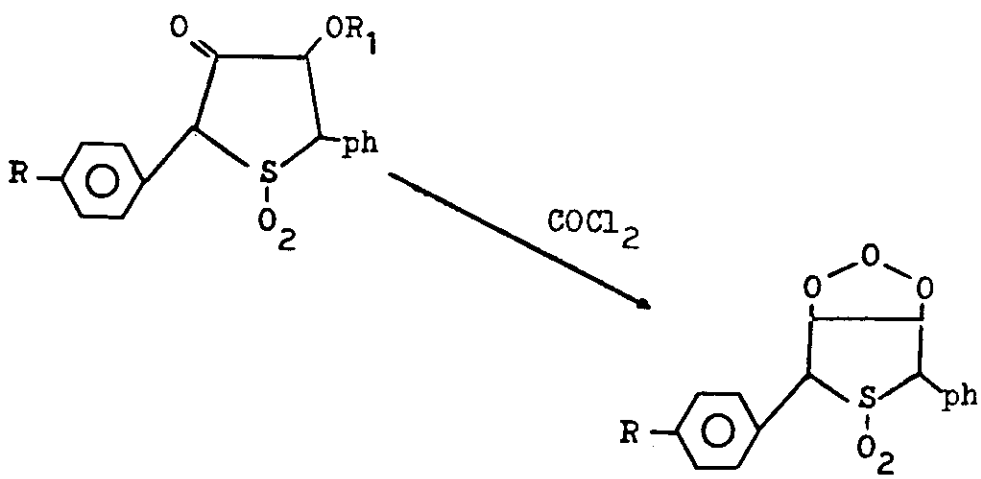
2,4-Dihydroxy-4-vinylbenzophenone was polymerized with azo-bis-isobutyronitrile as initiator; radical copolymerizations with methacrylic acid and styrene were also

accomplished [39]. In polymerizations with azo-bis-isobutyronitrile, no interference of the phenol groups of 2,4-dihydroxy-4′-vinylbenzophenone was observed. In copolymerization with styrene using benzoyl peroxide as initiator, the molecular weight of a copolymer containing 3 mol % 2,4-dihydroxy-4′-vinylbenzophenone was found to be significantly higher than that of styrene homopolymer prepared under identical conditions. This effect was also observed in the polymerization of styrene in the presence of a model compound, 2,4-dihydroxy-4′-ethylbenzophenone:





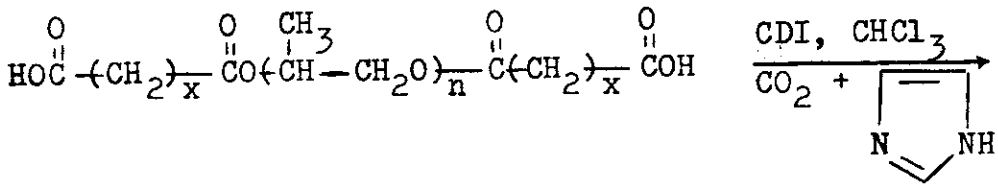
via the phenyl group were prepared as reagents for the synthesis of peptides and amides [42]. Thus, chloromethylated Merrifield resin (resin-$C_6H_4CH_2Cl$) was treated with $phCH_2SH$ to give resin-$C_6H_4CH_2SCH_2ph$ which was oxidized by H_2O_2 to give resin-$C_6H_4CH_2SO_2CH_2ph$, which was cyclized with $(CO_2Et)_2$ in EtOH containing Na to give thiophene (R=resin, R^1= H), which was esterified with $COCl_2$ to give cyclic carbonate (R = resin).

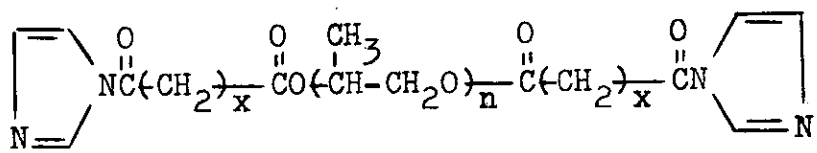


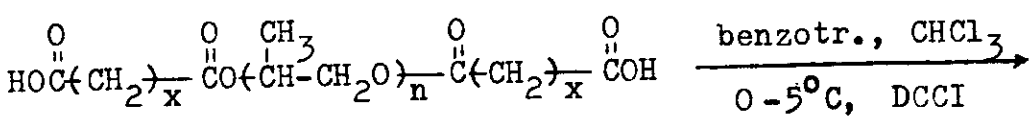
Cyclic carbonate

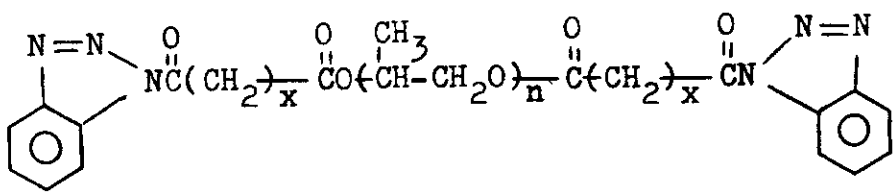
Succinic and glutaric half-ester of polypropyleneglycol have been prepared and transformed into the corresponding imidazolides and benzotriazolides. The exchange

reactions of the latter with hydroxylated and aminated compounds have been studied[43]. The main purpose of these studies was to develop new synthetic routes to oligomeric or polymeric derivatives of pharmacologically active compounds as follows:

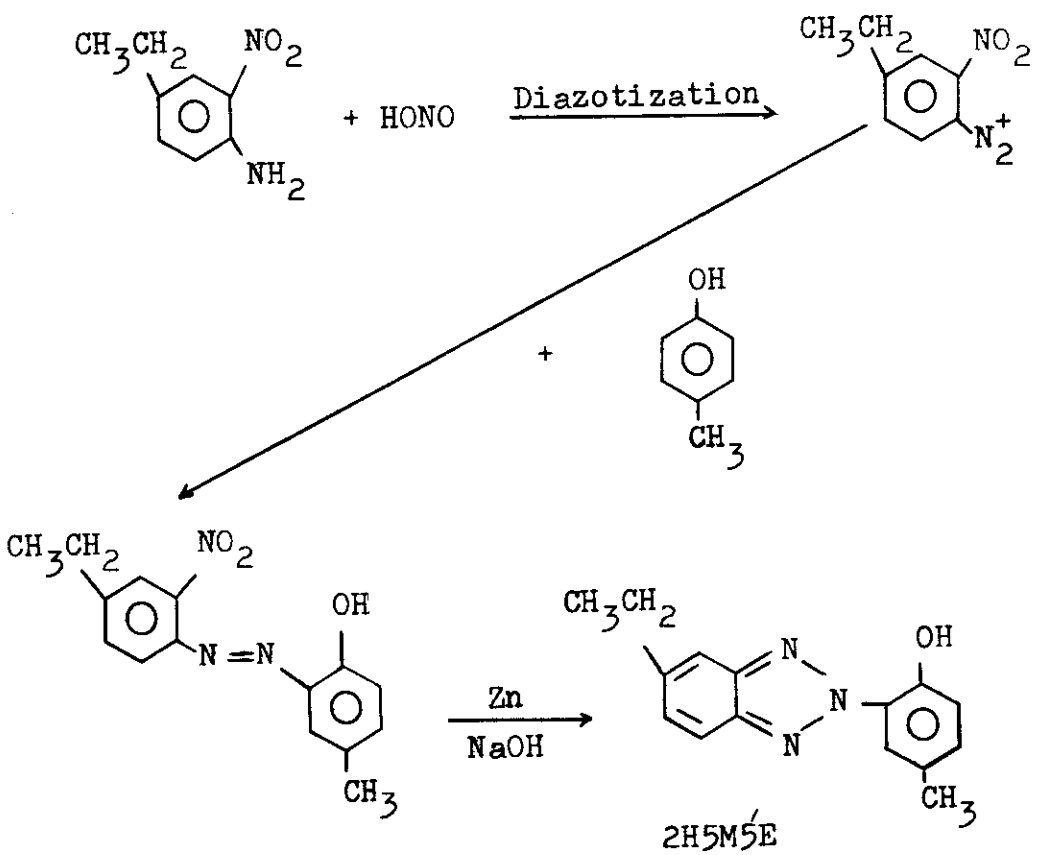




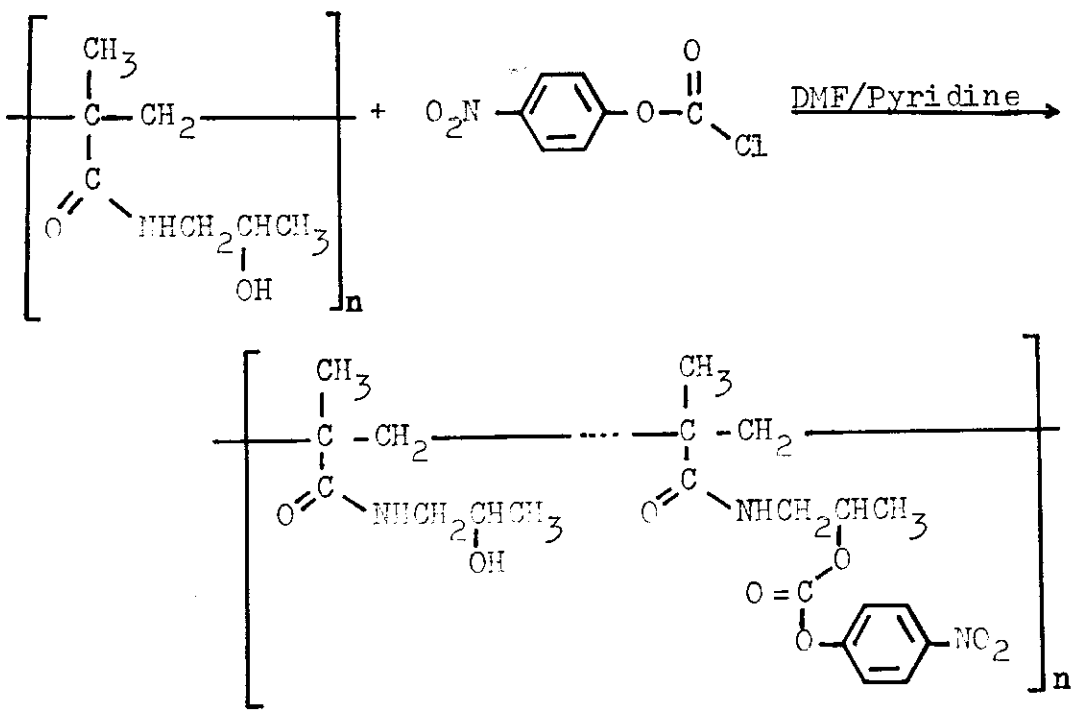




Yoshida et al.[44] studied the synthesis of 2(2-hydroxy-5-methylphenyl)-5-vinyl-2H-benzotriazole from 4-ethylaniline. Acetylation and nitration followed by hydrolysis gave 2-nitro-4-ethylaniline which was diazotized, condensed with p-cresol, and reduced to 2(2-hydroxy-5-methylphenyl)-5-ethyl-2H-benzotriazole. The ethyl group was transformed to the vinyl compound by bromination with N-bromosuccinimide and dehydrobromination of the 1-bromoethyl compound. The monomer 2(2-hydroxy-5-methylphenyl)-5-vinyl-2H-benzotriazole was polymerized and copolymerized with styrene, methyl methacrylate, and n-butyl acrylate:

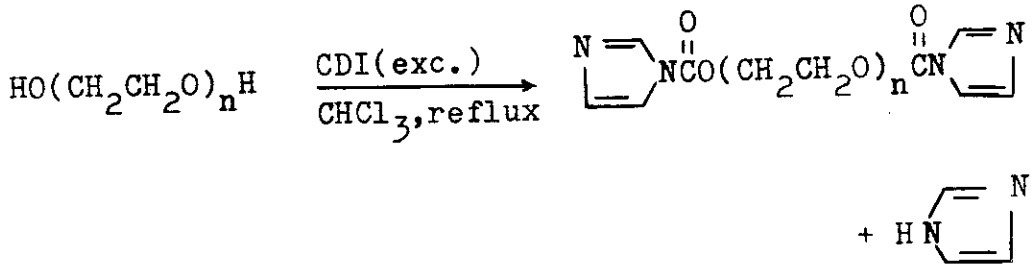


Lääne et al.[45] studied the reaction conditions for the activation of water-soluble, biocompatible poly[N-(2-hydroxypropyl)methacrylamide] by esterification with 4-nitrophenyl chloroformate as follows:

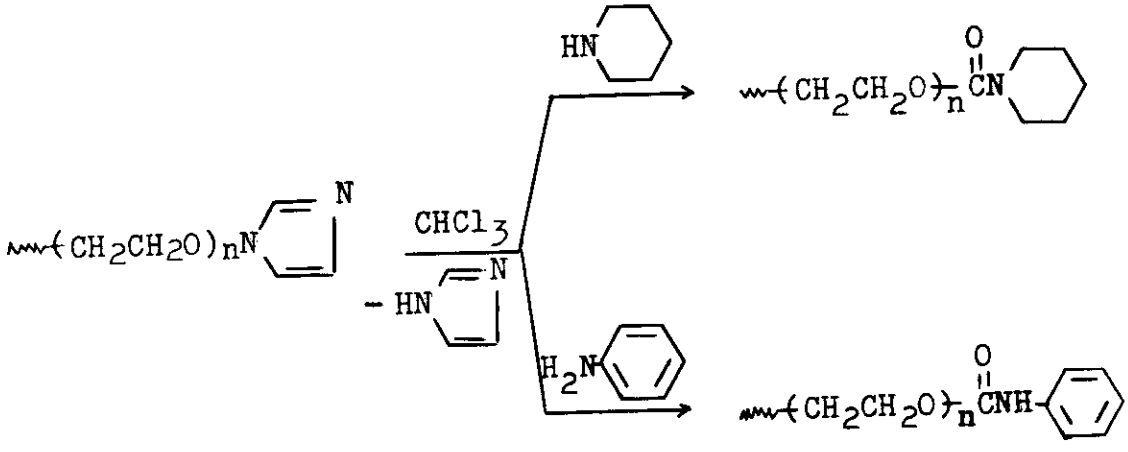


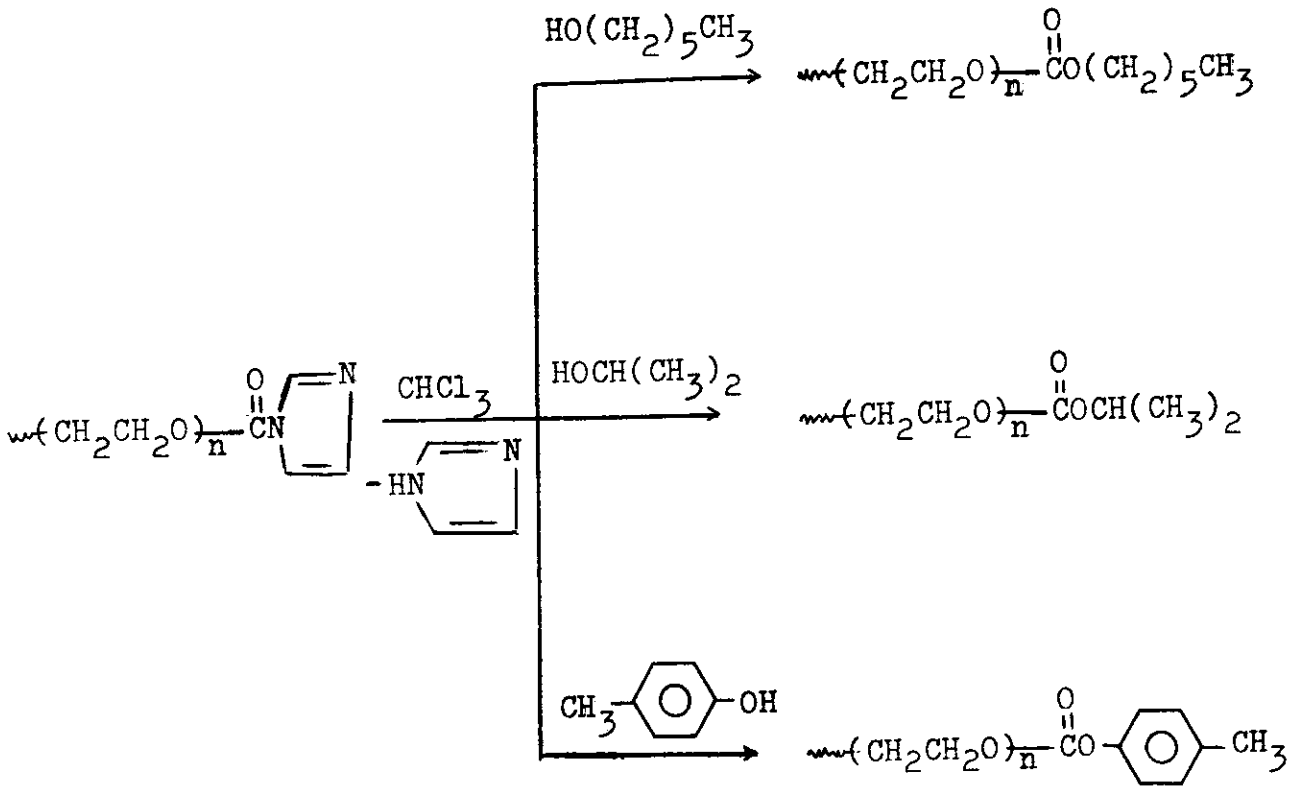
ω-(1-Imidazolyl) and ω-[4(5)-imidazolyl]alanoic acid were grafted onto poly(vinylamine) to give water-soluble catalysts of varying apolarity containing both hydrophobic and electrostatic binding sites for neutral and

charged substrates[46]. The influence of side-chain length, percent graft, and substitution in the imidazole ring are described. These grafts exhibited slower rates than poly[4(5)-vinylimidazole]. Among the esters examined were p-nitrophenyl acetate and 4-butanoyloxy-3-nitrobenzoic acid. Poly(ethylene glycol)s of molecular weight 200 and 1000 have functionalized by reaction with N,N-carbonyldiimidazole[47].

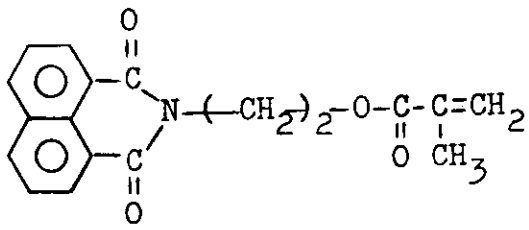


The resulting imidazolyl formates are able to react with model amines and hydroxylated compounds as:





2-1,8-Naphthalimidoethyl methacrylate was synthesized and polymerized[48]. The polymer obtained was observed to exhibit a weak monomer emission band at 380 nm and a broad emission band at 360 nm in 1,2-dichloroethane solution.



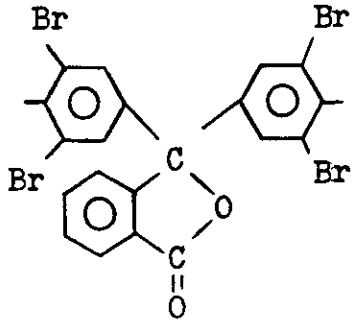
o-Methacryloyloxybonzoic acid was prepared by the reaction of salicylic acid with methacryloyl chloride using potassium carbonate as catalyst and acetone as solvent in the presence of a little amount of hydroquinone. The monomer was polymerized at different temperature from 30—120°C, using 2,2′-azo-bis-isobutyronitrile (AIBN) (0.3 mol %) and acetone or benzene as solvents[49].

New flame-retarding epoxy is synthesized by reacting 3′,5′,3″,5″-tetrabromophenolphthalein (TBPP) with epichlorohydrin and characterized in comparison with commercially available tetrabromobisphenol-A (TBBA) epoxy on their flame retardancy and thermostability[50]. TBPP epoxy show better results in promoting flame resistance than TBBA epoxy. However, TBPP epoxy exhibits a greater effect on thermal decomposition temperature. The order of char yield at 800°C under nitrogen for the cured products is TBPP epoxy > phenolphthalein (PP) epoxy > TBBA epoxy.

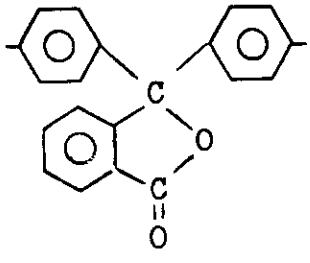
$$HO\text{-}R\text{-}OH + Cl\text{-}CH_2\text{-}CH\text{—}CH_2 \xrightarrow[NaOH\ (aq.)]{100\text{-}110^{\circ}C}$$

$$CH_2\text{—}CH\text{-}CH_2\text{-}[O\text{-}R\text{-}O\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}O]\text{-}R\text{-}O\text{-}CH_2\text{-}CH\text{—}CH_2$$

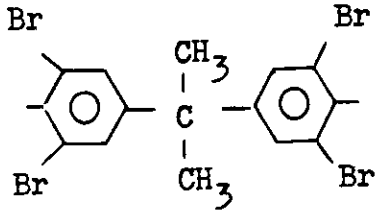
where:

R = 

(TBPP-Epoxy)



(PP-Epoxy)



(TBBA-Epoxy)

AIM OF THE PRESENT WORK

One of the most interesting topics in the field of pharmacologically active polymers is the preparation of polymeric drugs in which drugs are attached to the polymeric backbone via covalent bonds with limited stability to biological environments. If the drug molecule contains hydroxyl- or amino groups, the polymeric drugs are best prepared by reacting the drug with presynthesized polymer with functional side groups able to react selectively with above groups, giving ester or amido bonds. It was aimed to determine the optimal general condition for the synthesis and polymerization of some new monomeric phthalimides as well as the exchange reactions of their polymers with some aminated and hydroxylated compounds as a model compounds. Free radical copolymerization is a method of modifying the properties of polymers. The incorporations of higher properties of functional monomers and its better distribution within the polymer chain can be achieved through fundamental studies on copolymerization parameters under specified reaction conditions. It was also aimed to estimate the copolymer composition from ^{1}H NMR measurments and to determine the monomer reactivity ratios for copolymerizations of phthalimide monomers with methyl acrylate, methyl methacrylate and

acrylonitrile. It was also aimed to prepare terpolymers involving activated monomer as well as acrylonitrile to illustrate the variation of both instantaneous and average terpolymer composition on the basis of determined monomer reactivity ratios. Thus, it may be concluded that the new monomers described in this work may be useful for preparation of polymer-adducts of biomedical and pharmaceutical interest.