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POLYMERS AND COPOLYMERS OF VINYL MONOMERS WITH BLOCKED ISOCYANATE GROUPS: SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

The polymerization of vinyl monomers containing blocked isocyanate groups is reported. The blocking agents for the isocyanate groups of 2-isocyanato methacrylate were phenol, propanone oxime, benzophenone oxime, and ϵ -caprolactam. The $^1\text{H-NMR}$ and IR spectra of these polymers are discussed. Copolymerization reactivity ratios of the vinyl monomer blocked by phenol with styrene and methyl methacrylate have been determined. Glass transition temperatures of these polymers have been determined by differential scanning calorimetry. The homo- and copolymers were crosslinked in the presence of ethylene diamine, and the gels obtained were examined by IR spectra.

INTRODUCTION

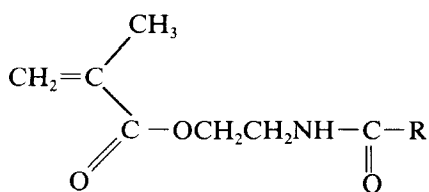
With the increasing interest in isocyanato-based systems for urethane coatings and adhesives, the availability of polymers containing vinyl isocyanate group is very attractive. The main chemical feature of isocyanates is their high reactivity toward nucleophiles such as alcohols, phenols, and amines. However, in certain situations this high reactivity can pose problems, particularly toward moisture. The reactivity can be reduced by conversion into derivatives, called "blocked isocyanates," which do not react with water at ambient temperature, but at higher temperatures either re-form the parent isocyanate or undergo displacement reactions; for example, formation of carbamates with alcohols and ureas with amines.

This work consists of the homo- and copolymerization of monomers with blocked isocyanate functions, previously synthesized and characterized [1]. Copolymerizations were carried out with styrene or methyl methacrylate. These copolymers have been prepared in view of future work involving the formation of tridimensional systems by the addition of difunctional molecules such as diamines or diols.

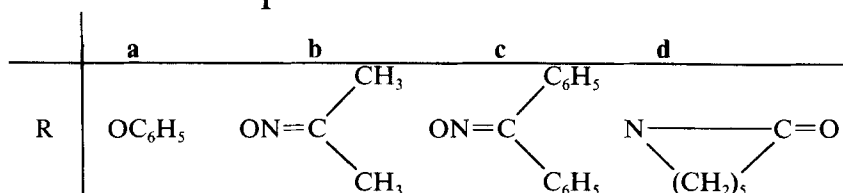
EXPERIMENTAL

Materials

The monomers used had the following formula:



1



They were synthesized as previously described elsewhere [1]. The methyl methacrylate was distilled over calcium hydride just prior to polymerization. The styrene was distilled over sodium wire and used immediately.

Instrumental

The monomer compositions of each copolymer were calculated from the results of elemental analysis (C, H, N, O).

The IR spectra were recorded on a Perkin-Elmer 983 IR Spectrometer, with KBr pellets. The proton NMR spectra were recorded on a Bruker AW60 NMR Spectrometer at 60 MHz in CDCl_3 with TMS as the internal reference. The glass transition temperatures were determined by differential scanning calorimetry on a Perkin-Elmer DSC 4 in sealed capsules with a heating rate of 20 K/min under nitrogen. The mass of each sample was of the order of 10 mg.

Molecular weights were determined by GPC analyzing using THF as eluent and a refractive index detector. Polystyrene and PMMA standards were used for calibration.

Polymerizations

All polymerizations were performed in sealed evacuated tubes of 140 × 220 mm. The tubes containing monomer(s), initiator, and solvent were sealed after the usual freezing, thawing, and evacuating. The contents of each tube were precipi-

tated in a nonsolvent. The polymer was recuperated by filtration in a fritted funnel and reprecipitated a second time to purify from solutions in chloroform or acetone. The polymer was then dried under vacuum at 40°C for 48 h.

The typical method used for the homopolymerization of Monomers **1a**, **1c**, and **1d** is as follows: 0.5 mol monomer was added to 60 mL THF containing azobisisobutyronitrile (AIBN) (1% concentration in relation to monomer). The mixture was heated at 60°C for 3 h. The polymer product was then precipitated in methanol and dried.

For Monomer **1b**, 1.1×10^{-2} mol were added to 60 mL benzene containing dicyclohexyl peroxy carbonate (2% concentration in relation to monomer). The mixture was heated at 50°C for 2 h. The polymer product was then precipitated in heptane and dried.

The copolymerizations were performed in bulk with AIBN as initiator at 50°C with the methyl methacrylate-**1a** pair and at 70°C with the styrene-**1a** pair. In order to determine copolymerization reactivity ratios, the conversions were always kept below 10%. The copolymers were precipitated in methanol and dried.

The polymers are referred to by the abbreviations **Pa** to **Pd** according to the corresponding monomers **1a** to **1d**, and the copolymers of **1a** are referred to by **MPa** and **SPa** for the methyl methacrylate copolymer and the styrene copolymer, respectively.

RESULTS AND DISCUSSION

Monomers **1a** to **1d** were polymerized in solution in the presence of AIBN or dicyclohexyl peroxy carbonate at low temperature (50–60°C). The intrinsic viscosities were determined in THF at 30°C, and the average molecular weights were determined by GPC at room temperature using THF as eluent (Table 1). These results indicate that high molecular weight polymers are readily formed as in a conventional methyl methacrylate polymerization. The urethane does not interfere in the polymerization by way of chain transfer or retardation. The various copolymers of the blocked isocyanate methacrylate with MMA and styrene were also prepared under similar conditions. The homo- and copolymers were characterized in detail by the IR and NMR as follows.

TABLE 1. Intrinsic Viscosity and Molecular Weight of the Homopolymers

	Pa	Pb	Pc	Pd
$[\eta]^a$	23.2	3.02	13.6	15.5
$\overline{M}_n \times 10^{-3}$	130	10	75	110
I^b	2.5	1.8	2.2	2.2

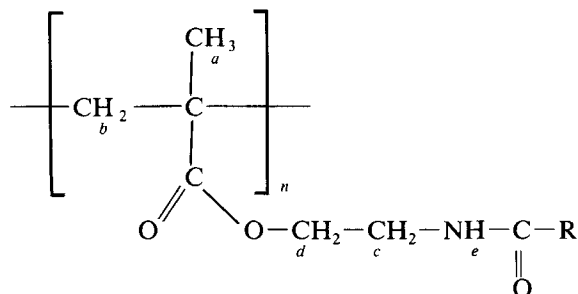
^aIn THF at 30°C, cm³/g.

^bPolydispersity $I = \overline{M}_w/\overline{M}_n$.

1. $^1\text{H-NMR}$ Characterization

1.1. Homopolymers

The chemical shifts (Table 2) of Homopolymers **Pa** to **Pd** reflect the following repeat unit:



Each polymer was identifiable by the chemical shifts of the blocked agents:

Pa: 5 aromatic protons at $\delta = 7.2$ ppm

Pb: 6 methyl protons at $\delta = 2$ ppm

Pc: 10 aromatic protons at $\delta = 7.3$ ppm

Pd: 10 methylene protons at $\delta = 1.8$ ppm (6H), $\delta = 2.8$ ppm (2H), and $\delta = 3.6$ ppm (2H)

The chemical shift of the proton related to the nitrogen (*e*) was dependent on the chemical environment. Systematic variation, in agreement with what has been reported in the literature [1, 4] occurred as the peak shifted from high field to low field corresponding to phenyl urethane and urea, respectively:

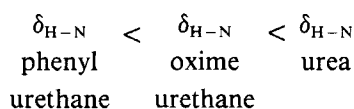


TABLE 2. ^1H Chemical Shifts of the Polymers **Pa** to **Pd** (δ in ppm in CDCl_3)^a

	Protons				
	a	b	c	d	e
Pa	0.91(m)	1.82(m)	3.40(m)	3.99(m)	6.11
Pb	0.80(m)	1.80(m)	3.60(m)	4.20(m)	6.80
Pc	0.80(m)	1.80(m)	3.60(m)	4.00(m)	6.85
Pd	0.80(m)	1.80(m)	3.50(m)	4.00(m)	9.50

^am = multiplet.

1.2. Copolymers

The $^1\text{H-NMR}$ spectra of Copolymers **MPx** and **SPx** consist of signals corresponding to their respective Homopolymers **Pa** to **Pd**, together with those of polystyrene and PMMA.

2. IR Characterization

The principal absorption bands of different groups are listed in Table 3 for the homopolymers and for the copolymers.

All the polymers show the following absorption bands:

- $\nu_{\text{N-H}}$: 3280 to 3410 cm^{-1} stretching vibration
1520 to 1550 cm^{-1} deformation vibration
- $\nu_{\text{C=O}}$: 1650 to 1750 cm^{-1} stretching vibration corresponding to carbonyls in ester, urethane, and urea groups
- $\nu_{\text{C-O}}$: 1030 to 1280 cm^{-1} stretching vibration of alkoxy groups in esters and urethanes

The absorption bands of N—H were broad for all the polymers, signifying the coexistence of free and hydrogen-bonded groups. In the spectra of Polymers **Pa** and **Pc**, these bands were centered at about 3410 cm^{-1} , which could show the predominance of nonhydrogen bonded NH [5].

In the **Pd** spectrum, the frequency of the N—H absorption band, 3280 cm^{-1} , is characteristic of the urea function.

The carbonyl absorption bands were broad, in agreement with literature results [6-9]. This confirms the existence of hydrogen bonding between the C=O and the N—H moieties.

In order to assign the absorption bands and to study the compatibility of the different urethane side groups and the polymer chains, the FTIR (Fourier transform

TABLE 3. Position of the IR Absorption Bands (in cm^{-1}) of —NH, —C=O, and —C—O— Groups in Polymers **Pa** to **Pd** and Copolymers **MPa** and **SPa** (KBr pellets)

	ν_{NH}	ν_{CO}	$\nu_{\text{C-O}}$
Pa	3350 (broad) 1528	1723 (broad)	1205-1163-1073
Pb	3412	1724 (broad)	1282-1150-1034
Pc	3410	1726 (broad)	1076-1246-1031
Pd	3280 1527	1726 (broad) 1660 (broad)	1080-1260-1030
SPa	3418 3340	1747 1725	1111
MPa	3432 (broad)	1728	1244

infrared) spectra of the **Pa** polymer and the **SPa** and **MPa** copolymers were recorded. The principal absorption bands are listed in Table 4.

2.1. The **Pa** Polymer

In the **Pa** spectrum, three absorption bands can be seen which correspond to carbonyls: 1699, 1718, and 1739 cm^{-1} . The band at 1699 cm^{-1} can be attributed to the H-bonded C=O groups, and the band at 1739 cm^{-1} to the free (or very weakly H-bonded) C=O groups in the urethane function. The band at 1718 cm^{-1} can be attributed to the weakly H-bonded C=O of the ester function, as the band corresponding to free C=O is generally found around 1725 cm^{-1} for methacrylates.

It can be seen that the difference in the frequencies of vibration between the free (or weakly H-bonded) C=O and the H-bond linked C=O is of the order of 40 cm^{-1} .

Two adsorption bands for N—H appear in the spectra: 3334 and 3339 cm^{-1} . These two band are found in the H-bond linked N—H range (3200 to 3400 cm^{-1}) [5, 6]. The difference, $\Delta\nu$, between these two bands is too small for them to be attributed with certitude, but in any case it can be supposed that they correspond to NH with hydrogen bonds of slightly different strengths established with carbonyls in the ester and urethane functions.

2.2. Copolymers

For the **MPa** copolymers, three absorption bands were observed. The bands at 1738 and 1734 cm^{-1} can be attributed to the weakly H-bonded carbonyls in the urethane function and the band at 1729 cm^{-1} to that of the ester function.

For the N—H, two absorption bands were seen at 3428 and 3393 cm^{-1} . The first was situated in the range of free N—H, and the second in that of H-bonded N—H.

The low percentage of urethane functions (<10%) can explain the weakness of the hydrogen bonds that are formed. It seems that hydrogen bonds occur only between the N—H and the carbonyls of the urethane functions, despite their theoretical dilution, which would signify the formation of aggregates in the polymer mass. These could result from the segregation between the polar urethane side groups and the main chain.

TABLE 4. Position of the FTIR Absorption Bands (in cm^{-1}) of —NH, —C=O Urethane and —C=O Esters Groups in Polymers **Pa** and Copolymers **MPa** and **SPa** (KBr Pellets)

	ν_{NH}	$\nu_{\text{C=O}}$ urethane	$\nu_{\text{C=O}}$ ester
Pa	3334 (H-bonded)	1739 (free)	1718
	3339 (H-bonded)	1699 (H-bonded)	
SPa	3411	1747 (free)	1727
		1725	
MPa	3393	1728	1729
	3428	1734	

For the **SPa** copolymers, three absorption bands were observed for the carbonyls: 1747, 1736, and 1727 cm^{-1} . The band at 1747 cm^{-1} is attributed to free carbonyls in the urethane function and that at 1736 cm^{-1} to a weakly H-bonded carbonyl. The band at 1727 cm^{-1} is attributed to the carbonyl in the ester function. For the N—H, only one absorption band is observed, at 3411 cm^{-1} , in the range of free N—H. The displacement of this band toward lower wavenumbers as compared to that observed in **MPa** could show the existence of weakly (or partially) H-bonded N—H.

With reference to Table 4, it can be deduced that for the **SPa** and **MPa** copolymers the carbonyl in the ester function does not participate in the formation of hydrogen bonds because of the dilution of the **Ma** monomer unit. The high absorption frequency (1747 cm^{-1}) observed for C=O in the urethane function in **SPa** signifies high compatibility between the phenyl urethane group in **Ma** and the styrene phase. The same phenomenon was not observed for the **MPa** copolymers. Their spectra showed absorption bands for carbonyl in the urethane function situated at lower frequencies (1738 and 1734 cm^{-1}). This would mean that despite the theoretical dilution of the urethane function ($[\text{Ma}]/[\text{MMA}] < 10\%$ in the copolymer), formation of aggregates occurs by incompatibility, aided by interchain H-bonding.

Solubility Characteristics. The Copolymers **MPa** and **SPa** and the Polymers **Pa**, **Pc**, and **Pd** are soluble in THF, dichloromethane, and chloroform; they are insoluble in hydrocarbon solvents (benzene, toluene, hexane, heptane) and in alcohols (methanol, ethanol).

The Polymer **Pb** is soluble in dichloromethane, chloroform, acetone, and alcohols (methanol, ethanol). Only the low molecular weight polymer chains (<10,000) are soluble in THF. They are insoluble in less polar hydrocarbon solvents.

3. Determination of Reactivity Ratios

The copolymerizations were performed by free radical polymerization of **1a** at 50°C with methyl methacrylate and at 70°C with styrene. The details of the monomer compositions are given in Table 5. In all cases the polymer conversion was kept below 10%. The reactivity ratios were determined by the method of Tidwell-Mortimer [10] and Fineman-Ross [11]. The copolymer composition is given by the equation of Mayo and Lewis [12] as

$$\frac{F_1}{F_2} = \frac{r_1 f_1^2 + f_1 f_2}{r_2 f_2^2 + f_1 f_2}$$

where f_1 and f_2 are the mole fractions of Monomers 1 and 2, and F_1 and F_2 are their instantaneous compositions (mole fractions) in the copolymer. Fineman and Ross (FR) rearranged this equation as

$$\frac{f_1}{f_2} \left[\frac{F_1 - F_2}{F_1} \right] = \frac{F_2}{F_1} \left[\frac{f_1^2}{f_1^2} \right] r_1 - r_2$$

TABLE 5. Details of Copolymerization and Copolymer Characteristics

Comonomer (M ₂)	Mole fraction × 10 ² of M ₁ in the feed	Mole fraction × 10 ² of M ₁ in the polymer	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	<i>I</i>
Styrene (St)	2.9	6.35	32	44	1.37
	4.2	9.10	32	43	1.34
	4.5	9.7	33	46	1.39
	5.5	11.7	28	47	1.68
	6.4	13.5	35	51	1.46
	7.0	14.65	25	43	1.72
	8.9	18.2	25	45	1.80
	9.9	20.2	28	46	1.64
	11.6	23.0	26	42	1.62
Methyl methacrylate (MMA)	1.8	2.18	260	500	1.97
	2.5	3.03	200	500	2.30
	3.0	3.63	400	600	1.50
	4.3	5.19	600	1000	1.66
	5.1	6.15	600	1100	1.83
	6.0	7.21	700	1200	1.80
	7.2	8.63	600	1100	1.83
	9.00	10.75	700	1300	1.85

A plot of the left-hand-side of the above equation versus $F_2/F_1 (f_1/f_2)^2$ gives a straight line with a slope equal to r_1 and an intercept equal to $-r_2$. The least-squares FR plots for the two monomers pairs are given in Figs. 1 and 2.

The equation of Mayo and Lewis is not linear, and its direct utilization to determine the reactivity ratios is tricky. The linear equation published by Fineman and Ross [11] in 1950 is still widely applied today. We have also calculated the reactivity ratios by using the method of nonlinear least squares of Tidwell and Mortimer [10] through a standard computerized procedure.

The monomer reactivity ratios calculated by the two methods are quoted in Table 6, and good agreement among the values obtained by the different methods can be seen.

An examination of the reactivity ratios reveals that **1a** enters preferentially into the polymer chain. The preference becomes more secure when the comonomer is styrene. Figure 3 shows the theoretical curves depicting the relative monomer feed composition for the copolymerizations. The enhanced reactivity of the urethane-containing monomer toward a given radical, as evident from both r_1 and r_2 values for either comonomers system, indicates that the urethane function does not have a significant effect on the reactivity of the vinyl bond compared to those values for the IEM-styrene pair. The urethane substituent on the ester group enhances the electronegativity of the carbonyl bond, facilitating a better conjugation of the urethane group with the radical formed, thereby stabilizing it. In other words, the

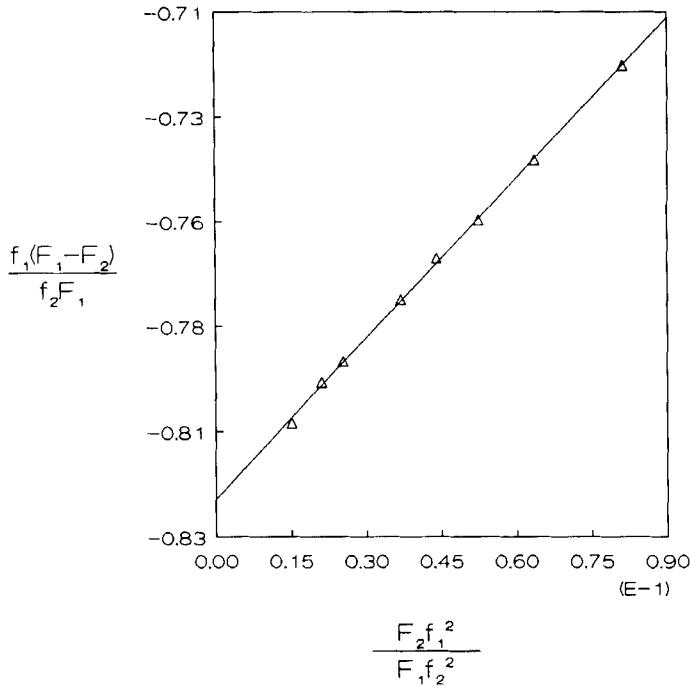
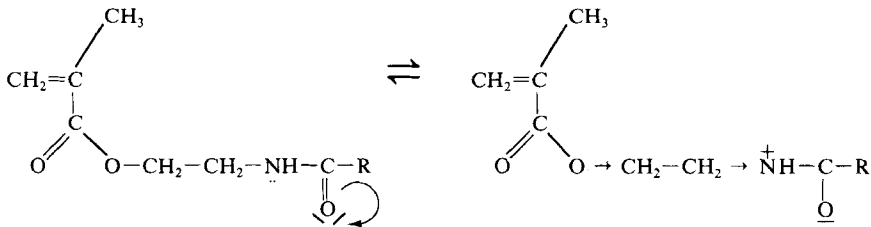
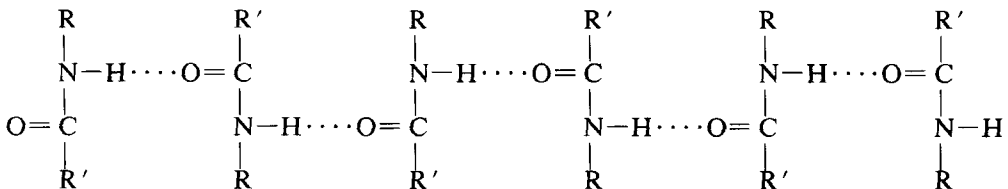


FIG. 1. FR plot for the blocked 2-isocyanatoethyl methacrylate-MMA pair.

+I effect of the substituent group enhances the monomer reactivity by way of better radical substitution:



The possibility of the association of the urethane-containing monomer is by way of H-bonding linkage which can give rise to a local enhancement of the concentration of this particular monomer.



Analyses of the polymer samples by IR have clearly shown such possibilities. Such monomer association can cause a pseudoenhanced reactivity and high r_1 (and low r_2) values. It is to be noticed that for the **1a**-styrene pair, the r_1 value is abnor-

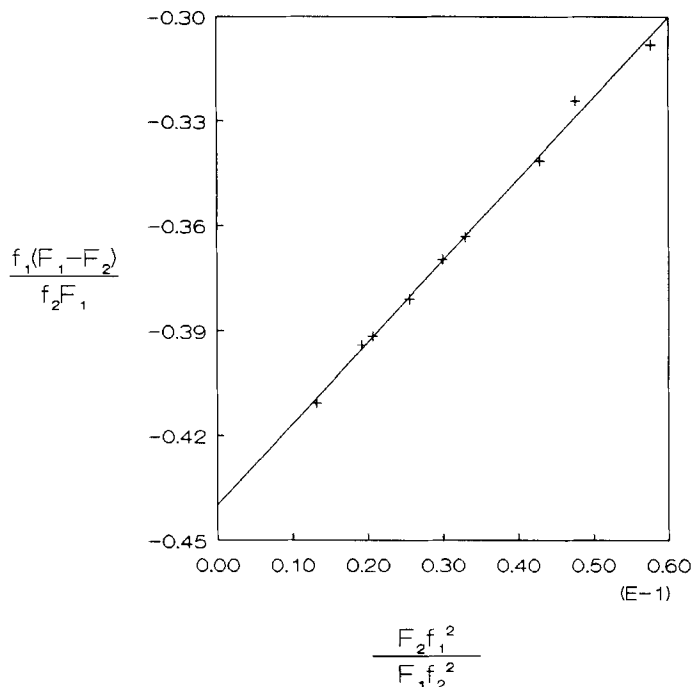


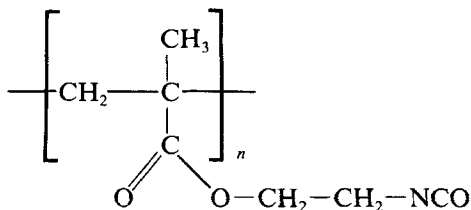
FIG. 2. FR plot for the blocked 2-isocyanatoethyl methacrylate-styrene pair.

mally high compared to those usually encountered for acrylate (or methacrylate)-styrene systems [13] (about 50 times). The superior reactivity of **1a** in this case cannot be explained by the enhanced monomer reactivity alone. The association phenomenon must be the more predominant factor.

The copolymerizations of **Mb**, **Mc**, and **Md** monomers with styrene and methyl methacrylate will be the subject of another publication.

4. Differential Scanning Calorimetry (DSC)

The glass transition temperatures (T_g) were measured for molecular weight $\overline{M}_n > 100,000$ and are shown in Table 7. All the polymers possess T_g values greater than that of the homopolymer of 2-isocyanato ethyl methacrylate ($T_g = 60^\circ\text{C}$):



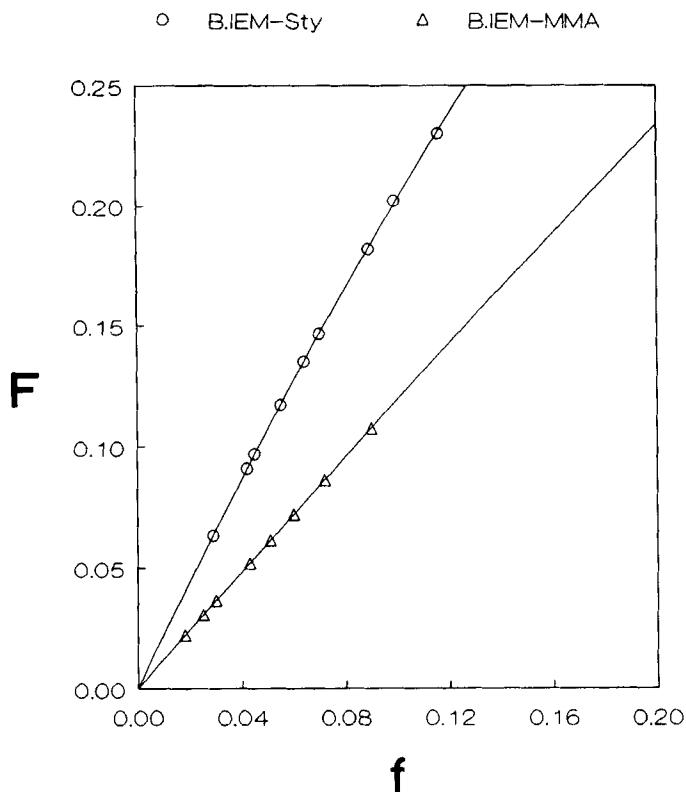


FIG. 3. Variation of the instantaneous copolymer composition of the comonomer feed composition. (—) Theoretical curves: (Δ) experimental points for blocked 2-isocyanatoethyl methacrylate-styrene couple, (\circ) experimental points for blocked 2-isocyanatoethyl methacrylate-MMA couple.

TABLE 6. Reactivity Ratios for the Blocked 2-Isocyanatoethyl Methacrylate (B.IEM) (M_1)-Styrene (M_2) and Blocked 2-Isocyanatoethyl Methacrylate (B.IEM) (M_1)-MMA (M_2) Pairs

Pairs	Fineman-Ross		Tidwell-Mortimer	
	r_1	r_2	r_1	r_2
Blocked IEM-St	2.33	0.44	2.32	0.44
Blocked IEM-MMA	1.22	0.82	1.21	0.81

TABLE 7. Glass Transition Temperatures of Polymers **Pa** to **Pd**

	Pa	Pb	Pc	Pd
$T_g, ^\circ\text{C}$	85	70	120 140	62

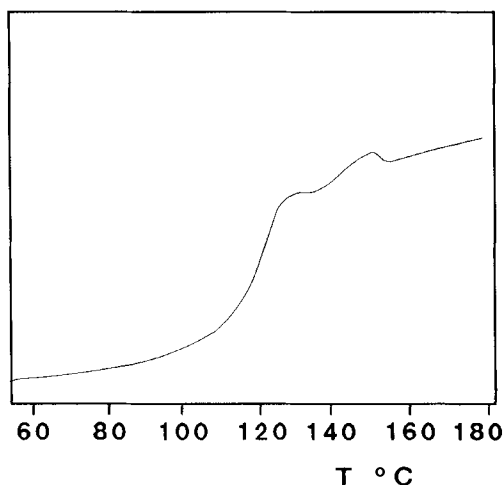


FIG. 4. DSC thermogram of poly-2-(iminobenzophenyl)oxycarbamoyl ethyl methacrylate (**Pc**). Heating rate: 20°C/min.

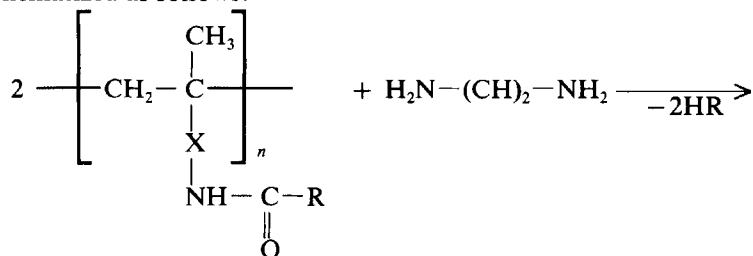
A general conclusion can be drawn: The blocking of the isocyanate increases the T_g of the corresponding polymers to a noticeable degree. This can be explained by 1) the rigidity [6] contributed by the urethane group due to its high cohesion energy (8.74 kcal/mol) [15], and 2) the formation of intermolecular hydrogen bonds between N—H and the carbonyl groups.

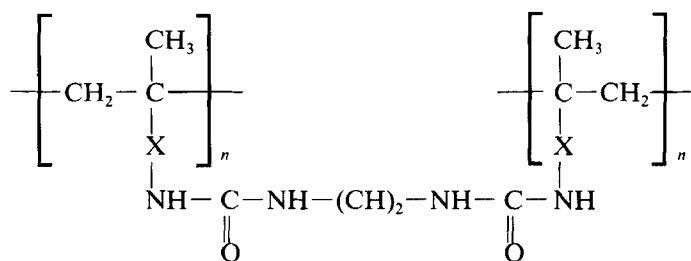
A larger increase in T_g was noted in the case of Polymers **Pa** and **Pc**, in which the urethane group includes an aromatic ring. It is known that aromatic systems are more rigid than aliphatic systems, notably in urethane [15] and amide [16] groups.

For **Pc**, two endotherms were observed on the DSC diagram (Fig. 4). It is supposed that the endotherm at 120°C corresponds to the glass transition temperature of the homopolymer. The one at 140°C is situated in the temperature zone of deblockage of the isocyanate function [15] and of the benzophenone oxime (mp = 140–143°C).

5. Crosslinking Tests

The polymers and copolymers obtained showed crosslinking in the presence of ethylene diamine. For the **Ma** polymers and copolymers, the crosslinking occurred at ambient temperature in THF in the presence of ethylene diamine; the appearance of microgels was instantaneous. It is known that polar solvents such as THF favor the deblocking reaction and that primary amines [2] rapidly react with isocyanates even at ambient temperature. The deblocking–crosslinking reaction can be schematized as follows:





The IR spectrum in KBr of the dried and pulverized gel showed the disappearance of the absorption band at 1740 cm^{-1} (characteristic of the urethane function) and the appearance of a band around 1650 cm^{-1} (characteristic of the urea function) (Fig. 5). The disappearance of the band at 1740 cm^{-1} , which converges with that at 1726 cm^{-1} (ester function), is deduced from the decrease in intensity and size of the band at 1726 cm^{-1} , and the relationship between the intensities of the absorption bands at 1726 and $1527\text{--}1560\text{ cm}^{-1}$. This relationship was reversed in the IR spec-

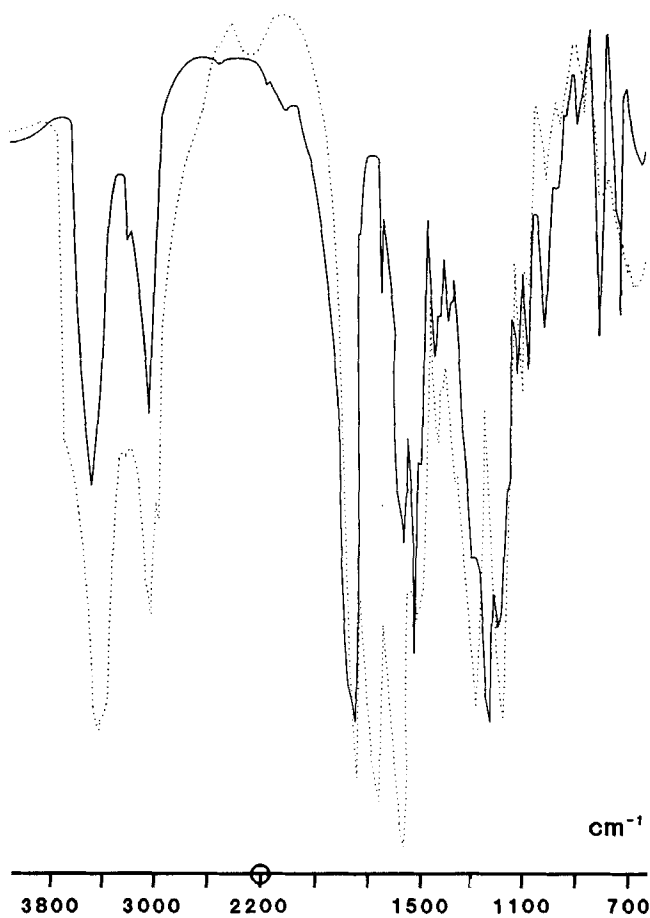


FIG. 5. IR spectra of poly-2-phenoxy carbamoyl ethyl methacrylate (**Pa**) in KBr pellet: (—) before crosslinking, (···) after crosslinking.

trum of PI as compared to that of the corresponding crosslinked polymer. The study of deblockage conditions in solution and in solid phase, as well as those of the gels obtained, will be the subject of another publication.

CONCLUSION

The polymers and copolymers of **a** with styrene and methyl methacrylate were characterized by ¹H-NMR and IR spectroscopy. Evidence for macromolecular association through the urethane linkage was seen in all cases using IR spectroscopy. The reactivity ratios of the copolymers were determined. In both cases the product $r_1 r_2$ is close to 1 ("ideal copolymerization"). The urethane-bearing monomer displayed enhanced reactivity.

The T_g values, measured by differential scanning calorimetry, were higher for polymers containing blocked isocyanate groups compared to those containing nonblocked polymers.

The polymers and copolymers are self-crosslinkable or crosslinkable in the presence of a diamine. The latter possibility was confirmed by IR.

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