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Synthesis and characterization of poly-(methyl methacrylate-co-*N*-4-bromophenyl maleimide)

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ABSTRACT: Radical copolymerization of methyl methacrylate (MMA, M1) and N-(4-bromophenyl) maleimide (N4BrPhMI, M2) in dioxane at 60 °C was performed with AIBN as initiator. Analysis of composition data points was carried out to a terminal model copolymerization. Using 1H, 13C and DEPT NMR measurements, the observed resonances were assigned. Glass transition temperatures were determined by DSC and a linear correlation was found between the Tg values and M2 content of the copolymers.

INTRODUCTION

Copolymers of N-substituted maleimides are mainly prepared to obtain new thermostable polymer materials [1]. These polymers are characterized with high temperature of vitrifying. The interest on the poly-maleimides grew also because of their unique properties as, e.g., physiological activity (antipyrene properties), optical and catalytic activity, etc. Based on these properties, copolymers of N-substituted maleimides are used also for preparation of membranes. Copolymerization of maleimides by free radical initiation has been studied extensively [2-7]. Complex model [8] was used to describe the copolymerization process of N-phenylmaleimide [9, 10]. Others argue against this interpretation [11, 12].

N-phenyl maleimide monomers with halogene substituent in the aromatic ring have been studied only in a few cases, e.g., the copolymerization of N-(4-chloro phenyl)-α-chloro maleimide with MMA has been described [4]. Anionic polymerization is a good method to obtain homopolymer [13-15].

In this paper composition, Tg and NMR spectra of copolymers obtained in the MMA/N4BrPhMI system are reported and analyzed.

EXPERIMENTAL

The monomer M2 has been prepared by condensation reaction of maleic anhydride with 4-bromoaniline. 17.2 g of 4-bromoaniline (0.1 mole) and 9.81 g of maleic anhydride (0.1 mole) were dissolved at room temperature in 200 cm^3 dried chloroform. From the homogeneous solution yellow crystals were slowly precipitated. After 1 hour, the solid mass was filtered off, yield: 25.65 g (95 %). 13.5 g (0.05 mole) of the half product monoamide and 0.30 g sodium acetate were dissolved in 100 cm^3 acetic anhydride and heated at 80 °C for two hours. The cooled solution was poured into 500 g of ice. The white precipitation was filtered off, and recrystallized from ethyl alcohol, yield: 91.5 %, melting point: 109-110 °C.

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MMA was purified by destillation.

The copolymerization was performed in dioxane solution under nitrogen atmosphere at 60 °C. Total monomer and AIBN concentration was 1.2 and $5.4*10^{-3}$ mole.dm^{-3}, respectively. The obtained samples were extracted with ethyl alcohol in a Soxlet apparatus.

The copolymer composition data were determined by elemental analysis and by 1H and 13C NMR measurements.

NMR spectra were taken on a Bruker SY 200 MHz instrument. Chloroform-d solution was used for copolymer samples with higher MMA content (samples: 1-6). Samples with higher M2 content were dissolved in acetone-d6 (7 and 8) or in DMSO-d6 (9 and 10). Quantitative 13C and DEPT experiments were run using the standard pulse sequences.

DSC studies were performed on a Mettler DSC-30 apparatus using 10 °C.min^{-1} heating rate.

RESULTS AND DISCUSSION

Table 1 summarizes the feed of monomers, copolymer composition and conversion data.

TABLE 1:
Monomer feed and Copolymer Composition Data Expressed as Mole Fraction of N-(4-Bromophenyl) Maleimide (M2).

Polymer No.	Conversion (wt%)	Monomer feed F_2	Copolymer composition f_2^a	f_2^b	f_2^c
1	24.07	0.101	0.068	0.072	-
2	24.28	0.200	0.129	0.138	0.145
3	23.46	0.307	0.179	-	-
4	24.39	0.400	0.243	0.242	0.250
5	23.42	0.500	0.352	-	0.333
6	22.29	0.603	0.378	-	-
7	20.06	0.697	0.411	-	-
8	14.53	0.801	0.518	0.503	0.508
9	38.99	0.898	0.726	0.733	-
10[d]	41.07	1.000	1.000	1.000	1.000
11[e]					

[a] Calculated from elemental analysis using the % nitrogen present

[b] Calculated from the 1H NMR intensities of aromatic and aliphatic region

[c] Calculated from the 13C NMR intensities of aromatic and aliphatic region

[d] Poly N4BrPhMI homopolymer prepared by free radical initiation

[e] Poly NPhMI homopolymer prepared by anionic initiation [13] (no data available)

1H NMR ANALYSIS

1H NMR spectra were assigned on the basis of copolymer samples with different composition. Figure 1 shows 1H NMR spectra of copolymer samples and that of homopolymer sample. (In the homopolymer prepared by anionic polymerization [13] there is no bromo substituent in the aromatic ring. It can be supposed that this fact may cause differences in the aromatic but not in aliphatic region.)

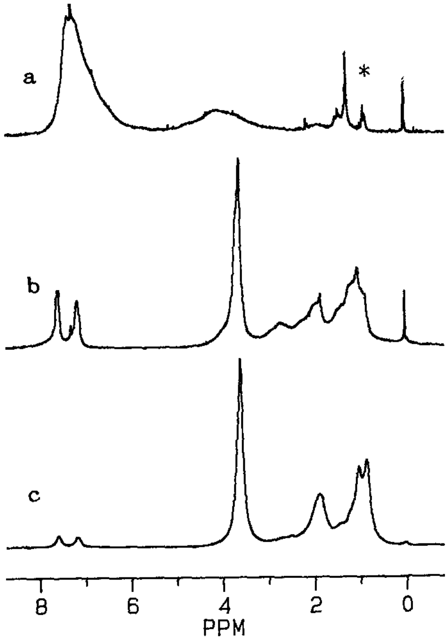

Figure 1: 1H NMR spectra of a: poly-N-phenyl maleimide homopolymer sample 11, b: copolymer 5, and c: copolymer 2.
Composition data see in Table 1.
(* impurity)

Solubility of sample 10 differs from sample 11. Sample 11 can be dissolved in CDCl3. However, sample 10 shows poor solubility even in DMSO-d6, consequently crosslinked structure can be supposed. Spectrum of sample 10 is similar to that of sample 11 but it is very noisy due to the low concentration.

The signal assignment of the spectra is the following:

δ=0.7-1.5 ppm	α-CH3 protons,
δ=1.6-2.3 ppm	CH2 protons,
δ=3.3-4.0 ppm	OCH3 protons,
δ=3.2-4.8 ppm	CH protons of the homopolymer sample,
δ=6.7-7.8 ppm	aromatic protons.

1H NMR spectra give very broad lines which are suitable for calculation of copolymer composition but not sufficient for determination of fine structure and monomer sequence distribution.

13C NMR ANALYSIS

Figure 2 shows decoupled 13C NMR spectra of homopolymer and copolymer samples. Figure 3 shows the 1H-13C coupled, APT spectrum and the DEPT CH-subspectrum of sample 5. The signal assignment of spectra is the following:

δ=17.0-21.5 ppm	α-methyl group,
δ=40.2-43.5 ppm	CH group connected to CH group of another M2 unit,
δ=45.2-45.8 ppm	quaternary carbon atom coupled to an M1 unit,
δ=49.2-49.8 ppm	quaternary carbon atom coupled to an M2 unit,
δ=52.0-52.3 ppm	OCH3 group,

δ=52.6-52.9 ppm	CH group coupled to a quaternary C atom,
δ=55.3-55.7 ppm	CH2 group,
δ=57.0-57.4 ppm	CH group coupled with CH2,
δ=122.6-133.0 ppm	aromatic carbons (not shown in Figure 2),
δ=175.1-178.5 ppm	carbonyl groups, both in M1 and M2 units.

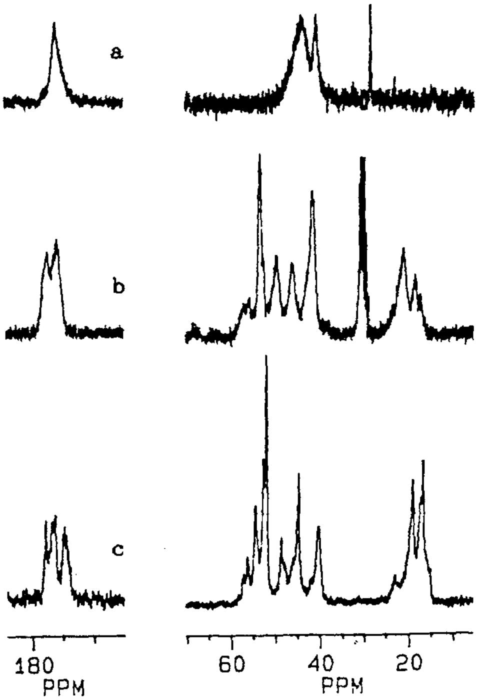

Figure 2: 13C NMR spectra of a: poly-N-phenyl maleimide sample 11, b: copolymer 5 and c: copolymer 2.

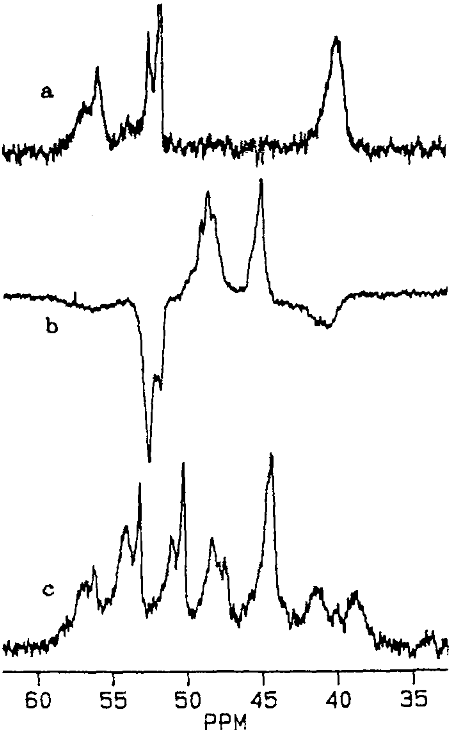

Figure 3: 13C NMR spectra of copolymer 5, a: DEPT CH-subspectrum, b: APT-spectrum CH_3 and CH groups are negative, c: 1H-13C coupled spectrum.

EVALUATION OF REACTIVITY RATIOS

The composition data obtained by NMR and elemental analysis were analyzed in terms of the terminal model using the high-conversion KT method [16]. A good linearity was obtained showing the applicability of the terminal model. Figure 4 shows the copolymer composition diagram.
The reactivity ratios are $r1=1.61\pm0.26$ and $r2=0.098\pm0.080$.
Figure 4 shows the copolymer composition diagram.

DSC ANALYSIS

The glass transition temperatures of copolymers with various composition were measured. A linear correlation was found in the investigated range of M2 content lower than 0.726. Copolymer sample 9 and homopolymers 10

and 11 showed no glass transition. Figure 5 shows the linear correlation of $f2^a$ vs. glass transition temperature.
Tg values of samples are summarized in Table 2.

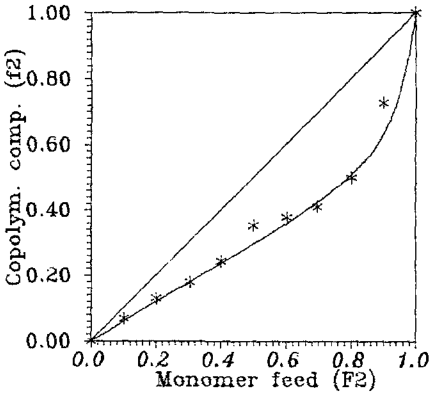

Figure 4: Copolymer composition diagram. The curve was calculated with the r-values determined.

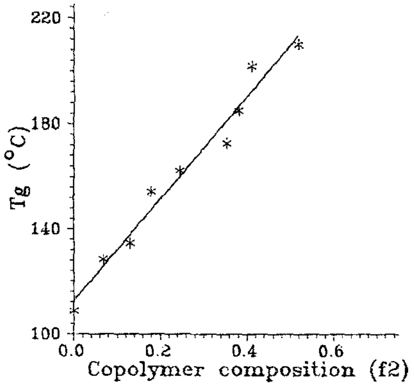

Figure 5: Correlation of copolymer composition ($f2^a$) and Tg values. (See Table 2.)

Tg values of samples are summarized in Table 2.

Table 2: Tg Values of Copolymer Samples

Polymer No.	Copolymer composition $f2^a$	Tg values (°C)
0	0.000	108.5
1	0.068	128.2
2	0.129	134.3
3	0.179	154.1
4	0.243	162.1
5	0.352	172.6
6	0.378	184.7
7	0.411	201.6
8	0.518	209.6
9	0.726	-
10[d]	1.000	-
11[e]	1.000	-

a, d, and e as in Table 1.

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