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3-CYCLOHEXYLOXY-2-HYDROXYPROPYL ACRYLATE–STYRENE COPOLYMERS: SYNTHESIS, CHARACTERIZATION, AND REACTIVITY RATIOS

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ABSTRACT

Copolymers of 3-cyclohexyloxy-2-hydroxypropyl acrylate (HHPA) with styrene were prepared by free-radical-initiated solution polymerization in 1,4-dioxane. ^1H and ^{13}C nuclear magnetic resonance techniques were used in the polymer characterization. Glass transition temperatures as a function of HHPA in copolymer changed from 76 to 17°C. The copolymer compositions were determined by elemental analysis and ^1H-NMR spectra. Reactivity ratios were calculated as $r_{\mathrm{HHPA}} = 0.37 \pm 0.34$ and $r_{\mathrm{styrene}} = 1.10 \pm 0.47$ from the Kelen–Tüdos equation, and $r_{\mathrm{HHPA}} = 0.31 \pm 0.08$ and $r_{\mathrm{styrene}} = 0.95 \pm 0.37$ from the Fineman–Ross equation.

INTRODUCTION

Functional (or reactive) polymers are produced either by chemical modification of preformed nonfunctional polymer or by direct copolymerization of the desired functional monomers with suitably chosen structural monomers [1]. Functional (meth)acrylates are monomers with an alkyl group having the desired reactive group such as hydroxyl, halogen, nitro, or amino. The hydroxyl group can be bonded on a polymer chain, such as in polyvinyl alcohol [2] and poly(3-hydroxyalkanoate)s

[3], or in a branch, such as 2-hydroxyethyl methacrylate [4] and 2-hydroxypropyl methacrylate [5, 6]. Copolymerization of functional (meth)acrylates with some other monomers provides a simple route for a type of functionality [7, 8].

In a previous study [9] we described the synthesis and characterization of 3-cyclohexyloxy-2-hydroxypropyl acrylate monomer and its homopolymer. The present paper reports the synthesis, nuclear magnetic resonance characterization, and determination of reactivity ratios and glass transition temperatures (T_g) for copolymers of 3-cyclohexyloxy-2-hydroxypropyl acrylate (HHPA) with styrene.

EXPERIMENTAL

Materials

Styrene was a product of Yarpet Turkish Chemical Company and was freed from inhibitor by dilute NaOH solution. Methanol, petroleum ether, and 1,4-dioxane (Aldrich) were used as received. Benzoyl peroxide (Aldrich) was recrystallized from a chloroform/methanol mixture. 3-Cyclohexyloxy-2-hydroxypropyl acrylate was prepared by the method reported in previous work [9].

Copolymerization

Appropriate amounts of HHPA and styrene with 1,4-dioxane and benzoyl peroxide (0.2% of the total weight of monomers) were placed in a dilatometric reaction tube. The mixture was deoxygenated by flushing with argon for at least 10 minutes. The tube was sealed by heating and immersed in a water bath at 60°C. Copolymerization was allowed to proceed to about 15% conversion. The copolymers were precipitated in an excess of methanol, methanol-water, and petroleum ether according to the composition of the copolymers. They were purified by dissolving in 1,4-dioxane and reprecipitating in the same nonsolvents. The copolymers were finally dried in a vacuum oven at 50°C for a few days.

^{1}H- and ^{13}C-NMR spectra of the copolymers were recorded in $CDCl_3$ with tetramethylsilane as the internal standard using a Varian-Gemini 200 MHZ spectrometer. DSC measurements were performed on a Shimadzu DSC-50 at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Copolymerization of HHPA with styrene in 1,4-dioxane solution was studied for a molar fraction of HHPA from approximately 0.1 to 0.9 in the feed. The conversions and the polymerization time varied between 8.5 and 15.0% and between 3.5 and 10.0 hours, respectively, in all copolymerizations. The amounts of monomeric units in the copolymers were determined by elemental analysis and integration of ^{1}H-NMR peaks. The results are presented in Table 1. ^{1}H-NMR spectra (Fig. 1) of Copolymers 2 and 5 show resonances at 7.3–6.4 ppm, corresponding to phenyl ring protons of styrene units. The signals at 4.2–3.1 ppm are due to $-COOCH_2$-

TABLE 1. Monomer Compositions in Feed and in Copolymer

Sample	Mol fraction of HHPA in feed (M_1)	Elemental analysis			Mol fraction of HHPA in copolymer	
		C%	H%	O%[a]	m_1[b]	m_1[c]
1	0.094	87.91	7.85	4.24	0.075	0.085
2	0.190	83.68	8.01	8.31	0.160	0.172
3	0.333	77.76	8.50	13.74	0.306	0.313
4	0.500	76.84	8.25	14.91	0.341	0.350
5	0.694	69.43	8.69	21.88	0.626	0.618
6	0.895	66.94	8.47	24.59	0.764	0.792

[a] Found by difference.
[b] Found by elemental analysis.
[c] Found by ^{1}H NMR.

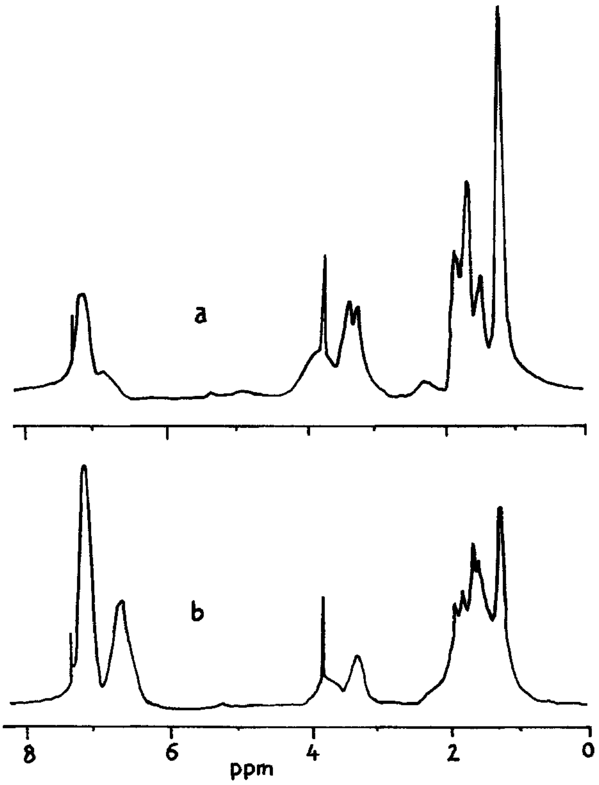
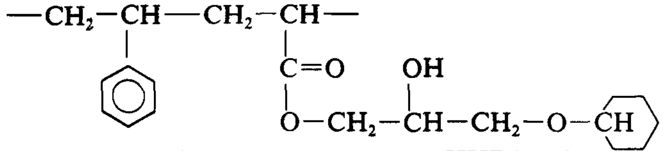


FIG. 1. ^{1}H-NMR spectra of poly(HHPA-*co*-styrene)s. (a) 62.6% (by mol) HHPA unit. (b) 16.0% (by mol) HHPA unit.



Styrene units HHPA units

CH(OH)CH_2OCH protons of HHPA. A group of signals between 2.3 and 1.1 ppm may be assigned to $-CH_2-$, $-CH-$ protons in the backbone, and cyclohexyl ring protons, except $-OCH-$ in HHPA units. Relative peak intensities are different in two ^{1}H-NMR spectra.

The proton-decoupled ^{13}C-NMR spectra of Copolymers 2 and 5 have the characteristic peak of the monomeric units (in Fig. 2). The ester carbonyl carbon of HHPA unit gave lines at 175.2–176.6 ppm. The quaternary carbon of the phenyl ring gave a less intense peak at 143.7 ppm. Ortho, meta and para carbons of the phenyl ring appeared at 127.8–128.5 ppm and 126.2–126.6 ppm, respectively. The peak at 63.0–70.0 ppm arises from $-CH(OH)CH_2OCH-$ in HHPA units. A less intense peak at 78.5 ppm, which is among the solvent peaks, is related to methylene carbon in the $-COOCH_2-$ group. A broad peak at 38.0–43.0 ppm may be assigned to methine and methylene carbons in the copolymer backbone. Sharp peaks at 24.0, 26.5, and 33.0 ppm arise from cyclohexane carbons of HHPA units in the copolymer, except for carbon bonded to oxygen.

A plot of copolymer composition versus glass transition temperature of the copolymer is shown in Fig. 3. T_g values of poly(HHPA) and polystyrene obtained under the same conditions with the copolymers were found at 8 and 97°C, respectively. T_g values of all the copolymers are between those of the homopolymers of the same monomers, but all copolymers have negative deviations relative to the additivity rule. When the mol fraction of HHPA in the copolymer changed from 0.075 to 0.764, T_g values changed from 17 to 76°C. Chain flexibility of poly(HHPA) is higher than that of polystyrene. This means that the free volume in poly(HHPA) is higher than that in polystyrene. Therefore, an increase of T_g as a function of the number of styrene units in the copolymer is an expected result.

Reactivity ratios were calculated by the graphical methods of Kelen–Tüdos (K-T) [10] and Fineman-Ross (F-R) [11]. The linear relations used are

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \qquad \text{(K-T equation)}$$

$$G = r_1 H - r_2 \qquad \text{(F-R equation)}$$

where $\eta = G/(\alpha + H)$, $\xi = H/(\alpha + H)$, $G = F(f - 1)/f$, $H = F^2/f$, $F = M_1/M_2$, $f = m_1/m_2$, $\alpha = (H_{max}H_{min})^{1/2}$, M_1 = mol fraction of HHPA in feed, M_2 = mol fraction of styrene in feed, m_1 = mol fraction of HHPA in copolymer, m_2 = mol fraction of styrene in copolymer, r_1 = reactivity ratio of HHPA, and r_2 = reactivity ratio of styrene.

The parameter α was found to be 1.738 from the highest (H_{max}) and lowest (H_{min}) values of H. K-T and F-R parameters calculated from the above equations using data in Table 1 are summarized in Table 2. The copolymer compositions obtained from elemental analysis were used in the calculation. Kelen-Tüdos (Fig. 4) and Fineman-Ross plots (Fig. 5) were drawn as η vs ξ and G vs H, respectively, obtained from data in Table 2. Linear equations of these plots as found by computer are

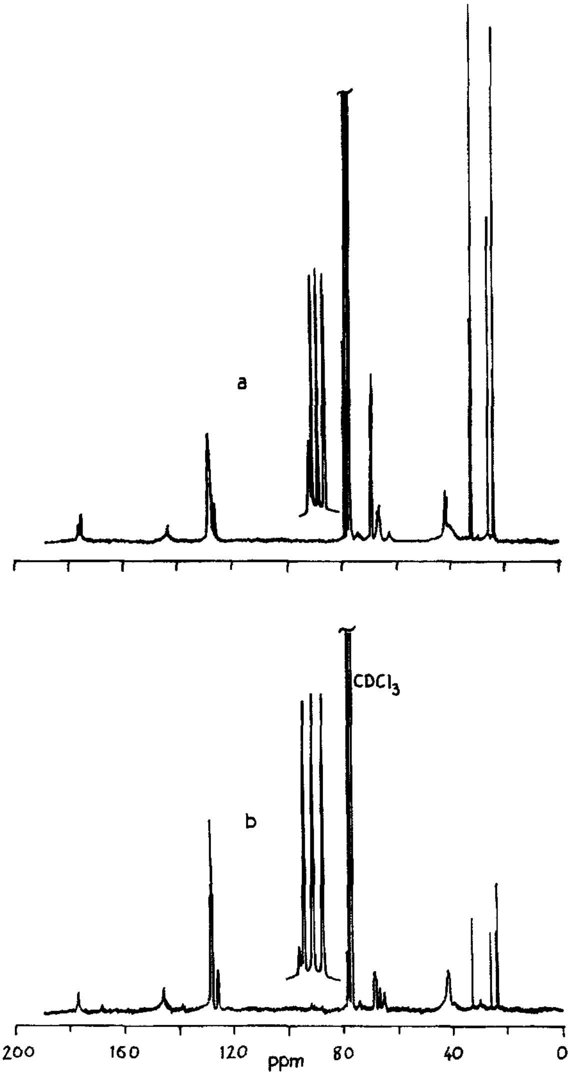


FIG. 2. ^{13}C-NMR spectra of poly(HHPA-*co*-styrene)s. (a) 62.6% (by mol) HHPA unit. (b) 16.0% (by mol) HHPA unit.

$$\eta = 1.00\xi - 0.63 \quad (\text{correlation coefficient, } R = 0.94)$$

$$G = 0.31H - 0.95 \quad (\text{correlation coefficient, } R = 0.98)$$

The reactivity ratios were calculated as $r_1 = 0.37 \pm 0.34$ and $r_2 = 1.10 \pm 0.47$ from the K-T linear equation, and as $r_1 = 0.31 \pm 0.08$ and $r_2 = 0.95 \pm 0.37$ from the F-R linear equation. The values of r_1 and r_2 indicate that this system has a behavior between ideal copolymerization and alternating copolymerization. While the reactivity of growing radicals with styrene ends is nearly the same toward styrene and HHPA, that of growing radicals with HHPA ends is somewhat higher toward styrene than HHPA.

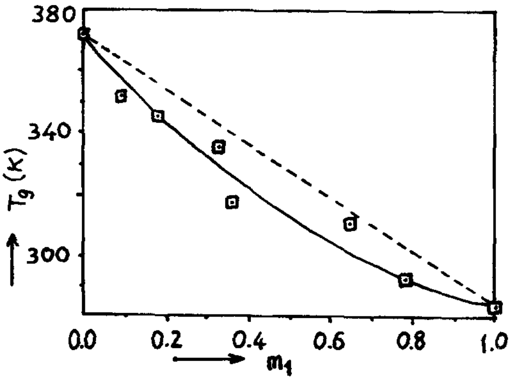


FIG. 3. Plot of glass transition temperature vs copolymer composition: m_1 = mol fraction of HHPA in copolymer.

TABLE 2. K-T and F-R Parameters for HHPA-Styrene System

No.	Ratio of feed composition, F	Ratio of copolymer composition, f	G	H	η	ξ
1	0.104	0.081	−1.180	0.134	−0.634	0.072
2	0.234	0.191	−0.991	0.287	−0.492	0.142
3	0.500	0.447	−0.618	0.559	−0.270	0.244
4	1.000	0.517	−0.935	1.935	−0.255	0.528
5	2.270	1.675	0.915	3.076	0.190	0.640
6	8.545	3.237	5.905	22.557	0.243	0.929

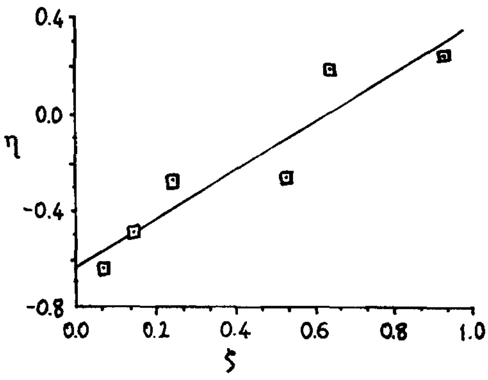


FIG. 4. Kelen-Tüdos plot.

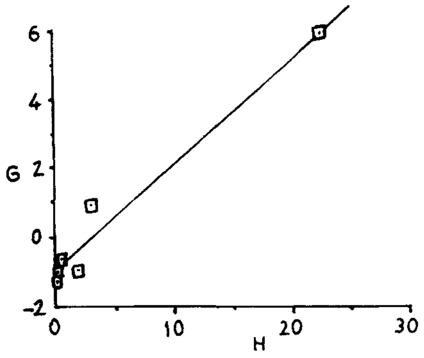


FIG. 5. Fineman-Ross plot.

CONCLUSIONS

Copolymerization of HHPA with styrene was performed in 1,4-dioxane using benzoyl peroxide. The copolymers were characterized by ^{1}H- and ^{13}C-NMR techniques. Glass transition temperatures of the copolymers were found to decrease with an increase in the mol fraction of HHPA. The copolymer compositions determined by ^{1}H-NMR spectra and elemental analysis were in agreement. The reactivity ratios determined for this system indicate that the reactivity of growing radicals with HHPA ends is somewhat higher toward styrene than HHPA.

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