COPOLYMERIZATION OF N-ACRYL-N,N'-DICYCLOHEXYLUREA AND N-METHACRYL-N,N'-DICYCLOHEXYLUREA WITH STYRENE

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COPOLYMERIZATION OF N-ACRYL-N,N´-DICYCLOHEXYLUREA AND N-METHACRYL-N,N´-DICYCLOHEXYLUREA WITH STYRENE

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ABSTRACT

N-Acryl-N,N´-dicyclohexylurea (A-DCU) homopolymers and copolymers with styrene (St) are prepared under the standard free-radical-initiated polymerization. Copolymers of A-DCU with St prepared under different monomer-to-monomer ratios in the feed, have random composition with an azeotropic point at a ratio of 0.73 (A-DCU) to 0.27 (St). N-Methacryl-N,N´-dicyclohexylurea (MA-DCU) does not homopolymerize, but copolymerizes with St to randomly composed copolymers. Reactivity ratios determined by the Kelen-Tüdös method are: r_1 (A-DCU) = 0.80; r_2 (St) = 0.50, and r_1 (MA-DCU) = 0.18; r_2 (St) = 4.84. All copolymers decompose under TGA conditions by a two step mechanism. In the first step, at a temperature of about 200°C separates cyclohexylisocyanate ($C_6H_{11}NCO$) under the formation of thermally stable poly(C_6H_{11}-acrylamido-co-St) and poly(C_6H_{11}-methacryl-amido-co-St) which decompose at a temperature of 450°C without the residue.

Key Words: Poly(acryl-dicyclohexylurea-co-styrene); Poly(methacryl-dicyclohexylurea-co-styrene); Poly(cyclohexylacrylamide); Poly(cyclohexylacrylamide-co-styrene); Poly(cyclohexylmethacrylamide-co-styrene); Reactivity ratios; Rate of copolymerization; Mechanism of thermal decomposition of copolymers.

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INTRODUCTION

In a previous paper from our Laboratory, it was shown that N-acryl-N, N'-dicyclohexylurea (A-DCU) homopolymerizes and copolymerizes with α-methyl-styrene in the presence of benzoylperoxide (Bz_2O_2), while N-methacryl-N,N'-dicyclohexylurea (MA-DCU) did not polymerize nor copolymerize with α-methylstyrene under the same experimental conditions [1]. In a continuation of this work, it was shown that both A-DCU and MA-DCU readily copolymerize in solution in the presence of Bz_2O_2 with styrene (St). In the present paper, will be described a comparison between the rate of copolymerization, reactivity ratios, and thermal stability of A-DCU and MA-DCU copolymers with St.

EXPERIMENTAL

Monomers and Copolymerization Conditions

Preparation of monomers A-DCU and MA-DCU is described in Reference [1]. Polymerization of A-DCU and MA-DCU was performed in vacuum-sealed 10 mL glass vials thoroughly degassed, filled with nitrogen before sealing and placed into an oil bath thermostated at 70°C. Homopolymerization and copolymerization of A-DCU with St were initiated with 0.5 wt% of Bz_2O_2 in butanone while MA-DCU was polymerized in dioxane or in butanone with 1.0 wt% of Bz_2O_2 at 70°C.

Physicochemical Measurements

^{1}H NMR spectra were obtained on a Varian EM 390 Spectrometer. The copolymer composition was determined by ^{1}H NMR spectroscopy in deuterated chloroform as solvent and by the elemental analysis. Differential scanning calorimetry was carried out on a Perkin-Elmer model DSC-2 with a scanning rate of 40°C min^{-1} in nitrogen with a sample size of 15 mg. Glass transition temperature was taken as the half-height of the corresponding heat capacity transition. The thermogravimetric analysis was carried out on a Perkin-Elmer TGS-2 Thermogravimetric System in a nitrogen stream with a heating rate of 10°C min^{-1}. Molecular weights based on calibration with monodispersed polystyrene standards (Polymer Laboratories) were determined by g.p.c. (Varian HPGPC Model 8500) using a set of 4 μ-styragel columns with THF as solvent at room temperature.

RESULTS AND DISCUSSION

As recently described by our Laboratory, monomers A-DCU and MA-DCU were prepared by condensation of acrylic or methacrylic acid with dicyclohexyl-

carbodiimide in tetrahydrofurane [1]. In the mentioned paper, it was shown that A-DCU homopolymerizes and copolymerizes with α-MeSt in butanone with Bz_2O_2 as initiator, while MA-DCU did not homopolymerize nor copolymerize with α-MeSt under the same experimental conditions.

In continuation of this work, it was found that A-DCU easily copolymerizes with St while MA-DCU can copolymerize with St only after a long heating of comonomers in butanone or in dioxane. Polymerization conditions and properties of copolymerization are listed in Tables 1 and 2 and copolymerization diagrams of both copolymerization systems are presented in Figure 1.

The data in Table 1 and Figure 1 show that copolymers of A-DCU with St prepared under different monomer-to-monomer ratios in the feed have random composition with an azeotropic point at ratio of 0.73 (A-DCU) to 0.27 (St) in the feed. Up to the azeotropic point at 0.73 molar fraction of A-DCU in feed, the content of A-DCU in copolymers is always higher than the content of St. Different results were obtained in the copolymerization of MA-DCU with styrene. As evident from the data in Table 2 under different ratios of comonomers in the feed, the content of MA-DCU in copolymers is always lower than the content of St (Figure 1 and Table 2).

In an attempt to homopolymerize MA-DCU in the presence of 1.5 wt% of Bz_2O_2 it was found that after 7 days of heating in dioxane or in butanone at 70°C only traces of insoluble precipitate are formed. By assuming that MA-DCU does not homopolymerize and that its reactivity ratio in the copolymerization with St equals, $r'_1 = 0$, the reactivity ratio of St (r'_2) was calculated on the basis of the terminal model by Equation 1 [2, 3, 4]:

Table 1. Polymerization Conditions and Properties of Poly (A-DCU-co-St); 0.5 wt% Bz_2O_2 in 1.5 mL of Butanone at 70°C

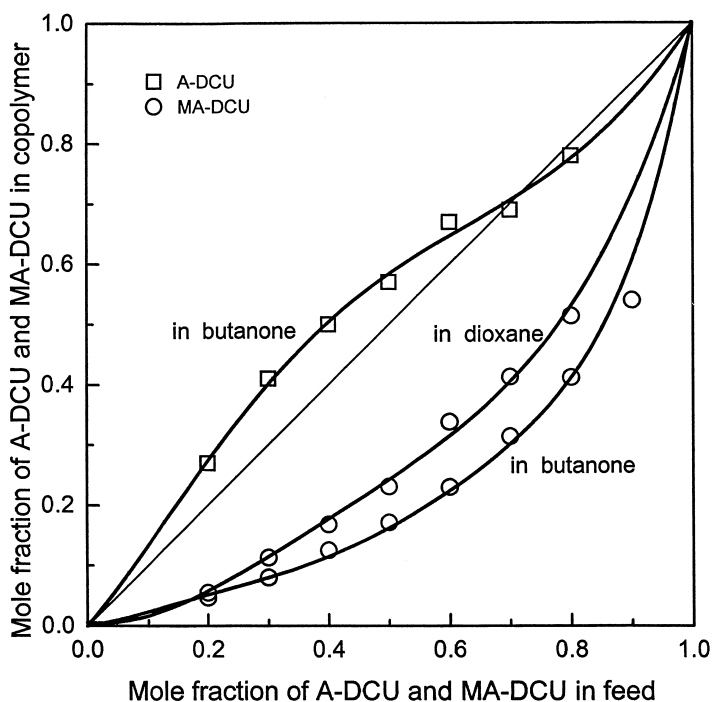| Molar Fraction of A-DCU			Polymer Time (hr)	Polymer Yield (g)	Convers. (%)	N (%)	T_g (°C)	Molecular Weight (g mol^{-1})	
In Feed	In Copolymer							$M_w \cdot 10^{-3}$	$M_n \cdot 10^{-3}$
	a)	b)							
0.2	0.27	0.27	6	0.0484	15.30	4.96	136	48.8	27.0
0.3	0.41	0.38	5	0.0476	13.55	6.52	141	56.3	27.2
0.4	0.50	0.52	4	0.0696	18.01	7.30	143	72.0	37.0
0.5	0.57	0.56	3	0.0706	16.38	7.85	153	78.6	39.7
0.6	0.67	0.70	2.5	0.0826	17.72	8.55	158	77.5	29.3
0.7	0.69	0.72	2.5	0.1156	22.63	8.64	168	83.7	33.9
0.8	0.78	0.77	2	0.0968	17.69	9.1	172	—	—

a) Based on nitrogen content.
b) Based on ^1H NMR data.

Table 2. Polymerization Conditions and Properties of Poly(MA-DCU-co-St), 1 wt% Bz_2O_2 in 1.5 mL of Butanone at 70°C

Molar Fraction of MA-DCU			Polymer Time (hr)	Polymer Yield (g)	Convers. (%)	N (%)	T_g (°C)	Molecular Weight (g mol^{-1})	
In Feed	In Copolymer							$M_w \cdot 10^{-3}$	$M_n \cdot \Sigma 10^{-3}$
	a)	b)							
0.2	0.047	0.041	16	0.0458	14.19	1.17	112	28.5	16.5
0.3	0.080	0.075	24	0.0583	15.49	1.89	115	16.3	10.0
0.4	0.125	0.125	24	0.0544	13.61	2.74	121	14.7	9.3
0.5	0.171	0.187	24	0.0526	11.81	3.52	130	12.0	7.8
0.6	0.255	0.282	68	0.0631	12.94	4.68	138	11.4	7.2
0.7	0.314	0.419	70	0.0708	13.29	5.39	142	10.8	7.0
0.8	0.412	0.519	72	0.0640	11.25	6.36	147	9.1	7.0
0.9	0.525	0.661	77	0.0360	5.92	7.25	—	—	—

a) Based on nitrogen content.
b) Based on ^{1}H NMR data.

Figure 1. Ratio of molar fraction of A-DCU (□) and MA-DCU (○) in the feed and in copolymers with St.

$$y' - 1 + r'_2 x' \qquad (1)$$

where y' denotes the ratio of St to MA-DCU in copolymers and x' is the ratio of St to MA-DCU in feed. From the plot of $y' - 1$ against x' in Figure 2, r'_2 was calculated as the slope of the straight line.

The reactivity ratios from Figure 2 are r'_2 (St) = 5.25 and r'_1 (MA-DCU) = 0.

Based on the copolymerization diagram in Figure 1 for the copolymerization of A-DCU and MA-DCU with St, the reactivity ratios are determined graphically with Kelen-Tüdös Equation 2 (Figure 3):
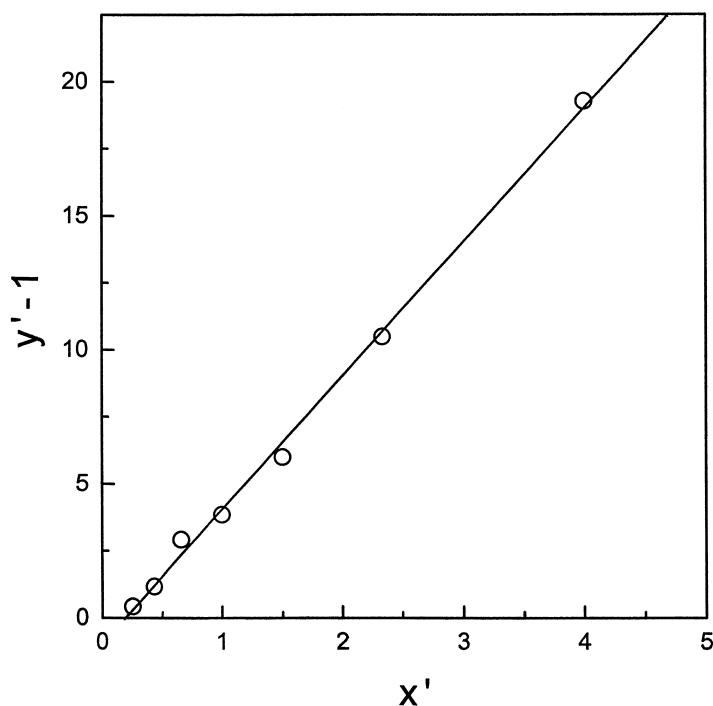
$$\eta = r_1 \xi - \frac{r_2}{\alpha} \left(1 - \xi \right) \qquad (2)$$

where η and ξ are functions of the molar fraction of monomers in the copolymers and in the feed respectively, and α is an arbitraty parameter [5].
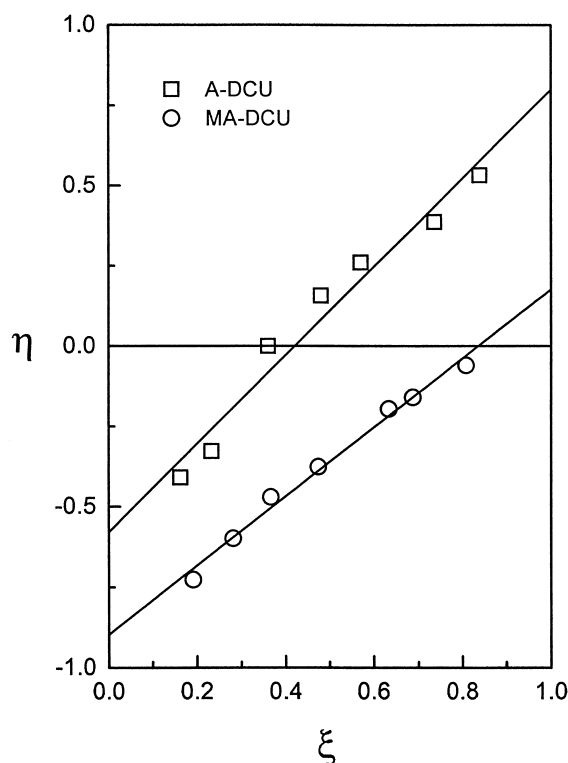
Numerical values of the reactivity ratios determined from the Figure 3 are:

r_1 (A-DCU) = 0.80; r_2 (St) = 0.50; α = 0.873 ($\square$)

r_1 (MA-DCU) = 0.18; r_2 (St) = 4.84; α = 5.397 ($\bigcirc$)

Figure 2. Plot of $(y'-1)$ versus x' in the copolymerization of St with MA-DCU in butanone at 70°C; 1 wt% Bz_2O_2 ; $(y'-1)$ is molar fraction of St/MA-DCU in copolymer and x' in feed.

Figure 3. Kelen-Tüdös diagram for calculation of reactivity ratios in the copolymerization of A-DCU with St (□) and MA-DCU with St (○).

In the copolymerization of MA-DCU with St, by the Kelen-Tüdös method, the reactivity ratio r_1 (MA-DCU) is smaller than one, while r_2 (St) is larger than one, thus indicating that MA-DCU favors cross propagation over homopolymerization, while St favors homopolymerization as opposed to cross propagation. It also shows that, since St is more reactive than MA-DCU, copolymers contain a higher proportion of St units.

It is further evident from Tables 1 and 2 that molecular weights of poly(A-DCU-co-St) increases with the increase of A-DCU in the feed, while molecular weight of copolymer of MA-DCU with St decreases with the increase of MA-DCU in the feed. One of the objectives of the present paper is the comparison of the initial rates of copolymerization of A-DCU with St and MA-DCU with St (Figure 4).

The data in Figure 4 indicate that the rate of copolymerization of A-DCU with St is faster than the rate of copolymerization of MA-DCU with St. It also shows that by increasing the amount of MA-DCU in the feed, the rate of copolymerization decreases, while in the copolymerization of A-DCU with St, the rate increases by the increase of A-DCU in the feed.

Thermal properties of poly(A-DCU-co-St) and poly (MA-DCU-co-St) are similar to those previously described in the decomposition of poly(A-DCU-co-α-
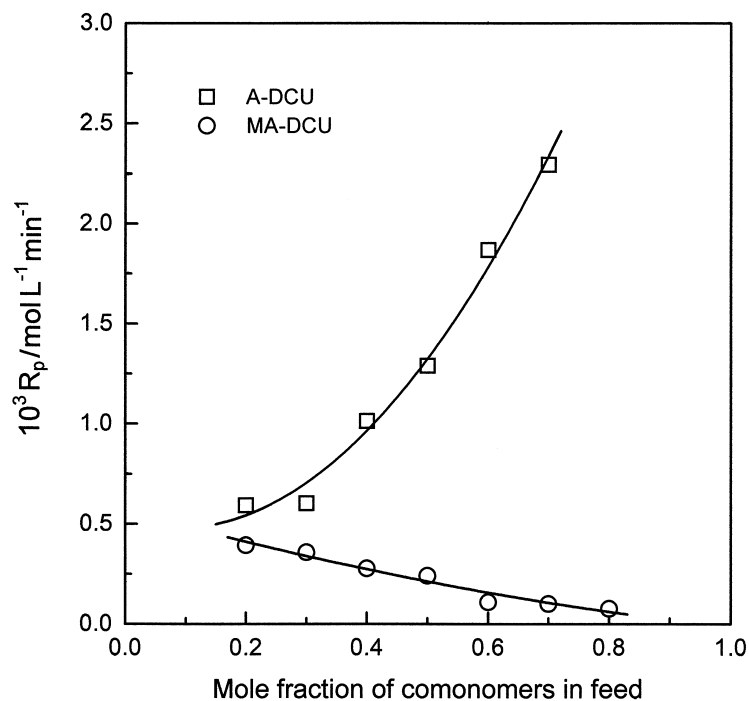
Figure 4. Initial rates of copolymerization of A-DCU (□) and MA-DCU (○) with St versus molar fraction of monomers in feed, in butanone.

MeSt) [1]. Both copolymers with St decompose by a two-step mechanism. In the first step, the copolymers are stable up to 200°C, when a volatile fraction identified as dicyclohexylisocyanate ($C_6H_{11}NCO$) separates. The residue stable up to 300°C decomposes by a one-step mechanism without residue (Figures 5 and 6). Assuming that the decomposition of studied copolymers follows the same path as the one previously evidenced in the decomposition of copolymer A-DCU with α-MeSt, the decomposition of copolymers of A-DCU and MA-DCU with St could be explained by the reaction illustrated in Scheme 1.
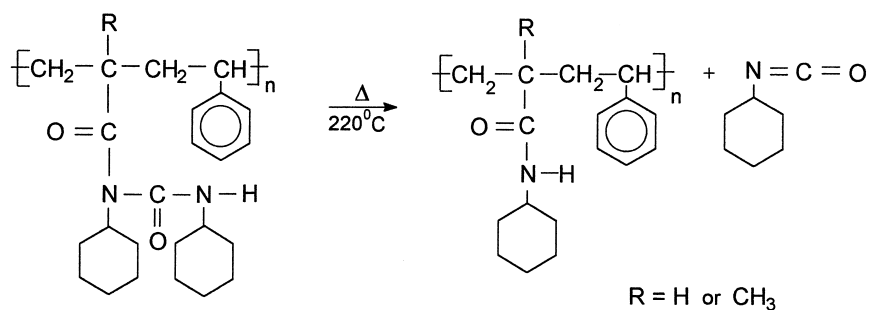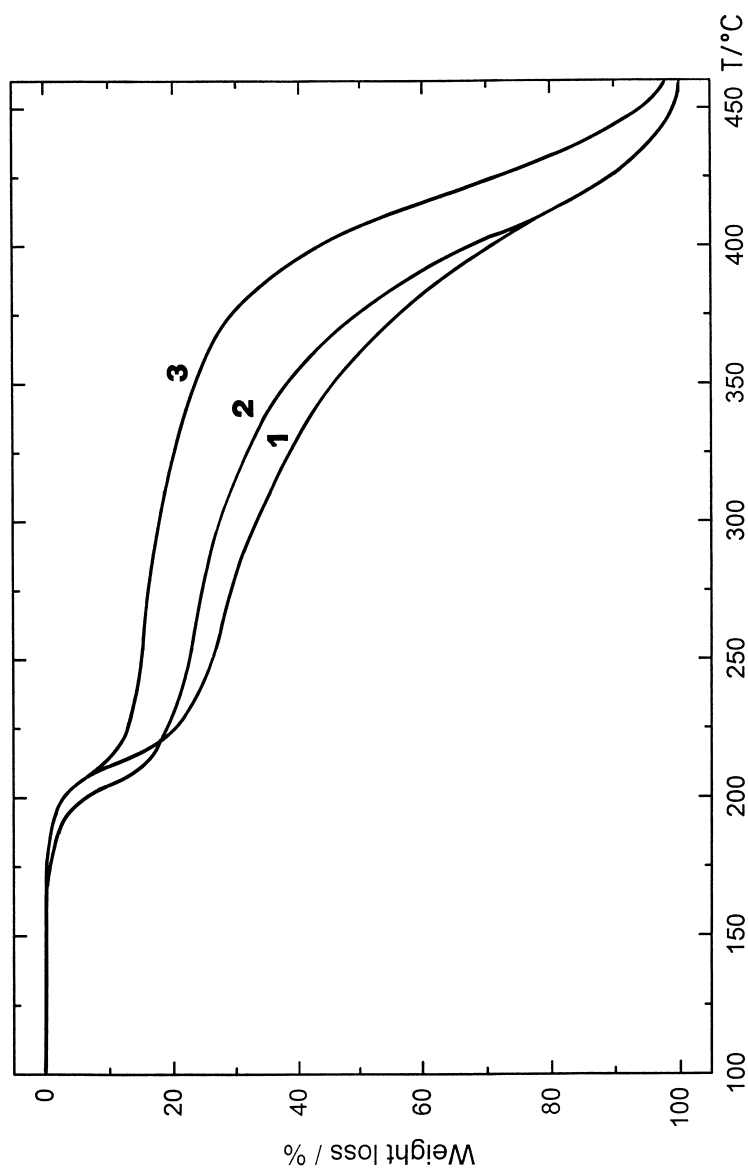

**Scheme 1.** Decomposition of poly[A-DCU (or MA-DCU)-co-St].
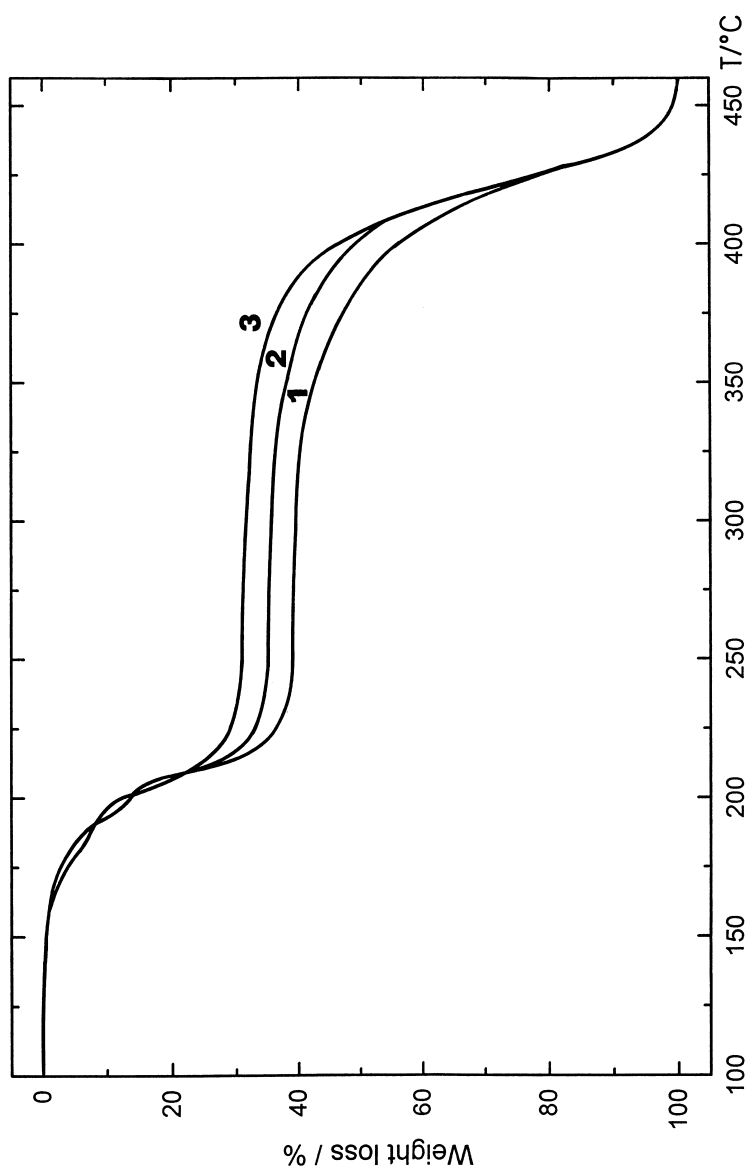
Figure 5. Thermograms of decomposition of poly(A-DCU-co-St) with molar monomers ratio in copolymers A-DCU:
St = 1) 0.78 : 0.22; 2) 0.67 : 0.33; 3) 0.50:0.50.

Figure 6. Thermograms of decomposition of poly(MA-DCU-co-St) with molar monomers ratio in copolymers MA-DCU: St = 1) 0.51 : 0.49; 2) 0.41: 0.59; 3) 0.28 : 0.72.

In order to prove the mechanism of thermal decomposition in Scheme 1, the following experiments were performed. A sample of 0.182 g of the copolymer 3 in Figure 5 was heated for 1 hour at 220°C in vacuum of 0.27 kPa (2 mm Hg). The volatile fraction (38% by weight) was identical with a commercial sample of $C_6H_{11}NCO$.

The amount of $C_6H_{11}NCO$ calculated from the loss of weight in TGA analysis of sample 3 from Figure 5 at a temperature of 250⁰C is 33%. The theoretical amount of $C_6H_{11}NCO$, in copolymer with molar ratio of A-DCU: St = 0.50:0.50 is 33%, which corresponds to the experimental value. The solid residue (0.144 g) after removal of $C_6H_{11}NCO$ was identified by elemental analysis and ^{1}H NMR spectroscopy as poly(C_6H_{11}-acrylamido-co-St); calculated for $C_{17}H_{23}NO$ (%): N, 5.45. Found: N, 5.98; Resonance signal values in ^{1}H NMR spectrum are at: 0.3-3.0 ppm (-CH_2- groups of cyclohexyl; -CH_2-; -CH- groups of acrylamide; and -CH_2- , -CH- groups of St); 3.4-4.0 ppm (-CH-N group of cyclohexyl); 4.0-6.5 ppm (-NH- group); 6.5-7.7 ppm (hydrogens of benzene ring in St). The same copolymers of C_6H_{11}-methacrylamide with St were also prepared and characterized by ^{13}C NMR and ^{1}H NMR spectroscopy by Pazhanisamy and coworkers [6]. Thermal stability of poly(MA-DCU-co-St) (sample 1 in Figure 6) was determined
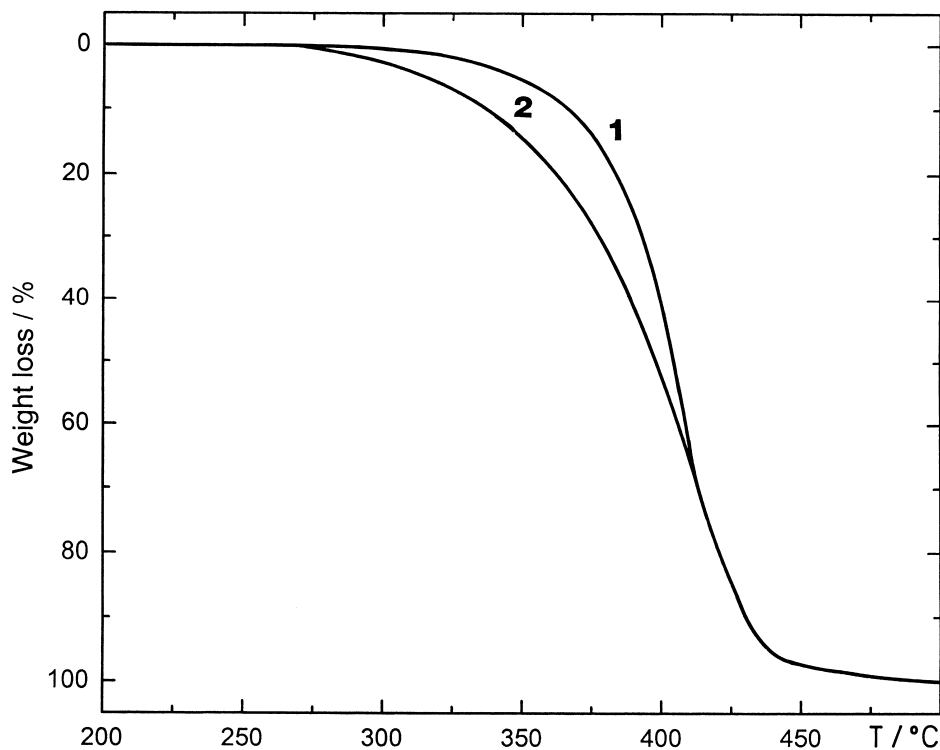

Figure 7. Thermograms of poly(C_6H_{11}-acrylamido-co-St) (1) and poly(C_6H_{11}-methacrylamido-co-St) (2).

in the same manner as previously described for a copolymer of A-DCU with St. After removal of a volatile fraction, the solid thermally stable copolymer, was collected and by elemental analysis and ^{1}H NMR spectroscopy, was identified as poly(C_6H_{11}-methacrylamido-co-St). Calculated for $C_{18}H_{25}NO$ (%): N, 4.83; Found: 3.74. ^{1}H NMR spectra show the presence of CH_3CH_2- group of methacrylamide. The TGA thermograms of thermostable residues of poly(C_6H_{11}-acrylamido-co-St) and poly(C_6H_{11}-methacrylamido-co-St) are illustrated in Figure 7.

Glass transition temperatures of poly(A-DCU-co-St) and poly(MA-DCU-co-St) prepared at different ratios of commoners in the feed are presented in Figure 8. By comparing T_g values in Figure 8 with the temperatures of degradation in Figures 5 and 6, it is evident that T_g's of all copolymers are within the thermally stable regions of copolymers, and that T_g's of poly(A-DCU-co-St) or poly(MA-DCU-co-St), linearly increase when the amount of A-DCU or MA-DCU in the feed is increasing.

Thermograms of thermally stable residues in Figure 7 are prepared from the copolymer 3 in Figure 5 (T_g = 143°C) and copolymer 1 in Figure 6 (T_g = 147°C). Thermally stable residues of these copolymer have T_g [poly(C_6H_{11}-acrylamido-co-St)] = 160°C and T_g [poly(C_6H_{11}-methacrylamido-co-St)] = 180°C, thus indicating that T_g's of thermally stable copolymers are higher than T_g's of poly(A-DCU-co-St) and poly(MA-DCU-co-St), respectively.
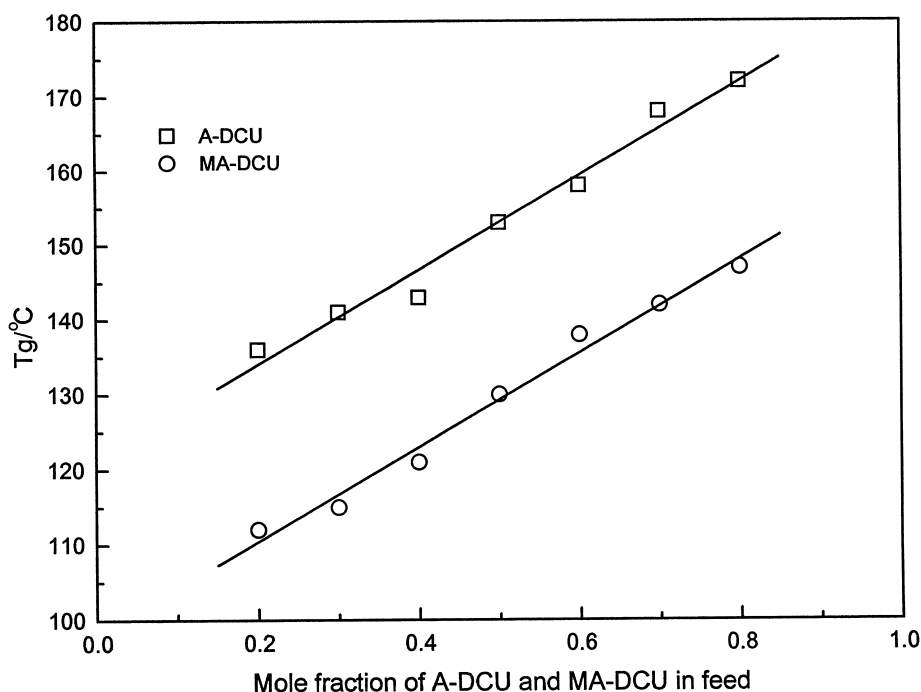
Figure 8. Glass transition temperatures of poly(A-DCU-co-St) (□) and poly(MA-DCU-co-St) (○).

CONCLUSION

Acryl-dicyclohexylurea (A-DCU) and methacryl-dicyclohexylurea (MA-DCU) readily copolymerize with styrene (St) under the free-radical-initiated polymerization with Bz_2O_2 in butanone or dioxane as solvent.

Copolymerization of A-DCU and MA-DCU with St is a statistical reaction with an azeotropic point at ratio of 0.73 (A-DCU) to 0.27 (St).

Molecular weights of copolymers prepared at equimolar ratios of comonomers in the feed are M_w (A-DCU-co-St) = 78600 g mol^{-1} and M_w (MA-DCU-co-St) = 12000 g mol^{-1}.

All copolymers decompose under the TGA conditions by a two-step mechanism. In the first step at a temperature of 220°C in nitrogen separates cyclohexylisocyanate ($C_6H_{11}NCO$) under the formation of thermally stable poly(C_6H_{11}-acrylamido-co-St) and poly(C_6H_{11}-methacrylamido-co-St). Glass transition temperatures of all copolymers are within the thermally stable region.

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