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Free-Radical Initiated Polymerization of N-methacryl-N,N′-diisopropylurea with Styrene

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Free-radical initiated copolymerization of N-methacryl-N,N′-diisopropylurea (MA-DiPrU) with styrene (St) was performed to low conversion by using dibenzoyl peroxide (Bz_2O_2) in butanone at 70°C. The copolymer composition was calculated on the basis of nitrogen content in copolymers. The reactivity ratios determined by the Kelen-Tüdös method are: r_1(MA-DiPrU) = 0.39 and r_2(St) = 1.03. In all cases, regardless of the monomer-to-monomer ratios in the feed, an excess of St was present in copolymers. Copolymers decompose under TGA conditions in nitrogen by a two-step mechanism. In the first step between 180°C and 250°C, isopropylisocyanate (iPrNCO) separates by degradation of diisopropylurea in the side chain. The thermally stable residue represents the copolymer of methacryl-isopropylamide (MA-iPrU) with St, which decomposes by a one-step mechanism between 280°C and 450°C.

Keywords methacryl-N,N′-diisopropylurea, styrene, poly(methacryl-isopropylurea-co-styrene), poly(methacryl-isopropylamide-co-styrene), thermal properties, thermal degradation, isopropylisocyanate

Introduction

In a series of recently published papers (1–6) we described the preparation of monomers, homopolymers, and copolymers, which contain dicyclohexylurea (DCU) or diisopropylurea (DiPrU) as a pending group. It was found that N-acryl-N,N′-dicyclohexylurea (A-DCU) readily homopolymerized and copolymerized with St and α-MeSt (1, 2). N-methacryl-N,N′-dicyclohexylurea (MA-DCU) can copolymerize with St only after a long heating of comonomers (2). During our studies, it was also shown that A-DCU and MA-DCU were copolymerized with ethylene-glycol dimethacrylate (EDMA) yielding crosslinked copolymers which thermally decompose by a two-step mechanism under the formation of cyclohexylisocyanate and nanoporous crosslinked copolymers of (met)acryl-N- cyclohexylamide with EDMA (3–5). Recently, we published the preparation of N-methacryl-N,N′-dicyclohexylurea, copolymerization with EDMA, as well as preparation of nanoporous copolymers of methacryl-isopropylamide with EDMA by thermal degradation of above mentioned copolymers (6). In those studies, we found

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quite different behavior of the copolymers containing diisopropyl group in comparison with the corresponding copolymers of DCU. In the present paper, n continuation of this work, we wish to describe the preparation of copolymers of methacryl-N,N′-diisopropylurea with styrene, at different monomer-to-monomer ratios in the feed, and their thermal behavior.

Experimental

Monomers

N-Methacryl-N,N′-diisopropylurea (MA-DiPrU) was prepared by condensation of diisopropylcarbodiimide (DiPrC) (Fluka, Buchs, Switzerland; purum) with methacryl acid (MAA) (Fluka, Buchs, Switzerland; purum) in THF (Fluka, Buchs, Switzerland; purum), as previously described (6). Styrene (St) (Fluka, Buchs, Switzerland; 99.5% puriss) was distilled before use.

Copolymerization

Copolymerization of MA-DiPrU with St was performed in thermostated glass vials under purified nitrogen. The poly(MA-DiPrU-co-St) were prepared by free-radical polymerization in butanone (Fluka, Buchs, Switzerland; purum) at 70°C with Bz_2O_2 (Fluka, Buchs, Switzerland; $\geq$97%). After the polymerization, the solution of copolymers was diluted with chloroform (Fluka, Buchs, Switzerland; $\geq$99.5%) and precipitated by a dropwise addition to methanol. The copolymers were filtered off and dried in vacuum at 80°C for 24 h.

The procedure applied for the copolymerization of MA-DiPrU with St at molar ratio of 0.5 to 0.5 in the feed was as follows: A mixture of 0.424 g (0.002 mol) of MA-DiPrU and 0.208 g (0.002 mol) of St in 2 mL of butanone with 2 wt% Bz_2O_2 was heated for 26 h at 70°C, under a steam of nitrogen. A copolymer yield of 0.1169 g (18.5 wt%) was obtained after precipitation in methanol from a chloroform solution and after drying in vacuum at 80°C for 24 h. Based on the nitrogen content, the copolymer contains 0.298 mol fraction of MA-DiPrU and 0.702 of St (Table 1). Under the same experimental conditions, the copolymers of MA-DiPrU with St at molar to molar ratios: 0.2/0.8; 0.3/0.7; 0.4/0.6; 0.7/0.3 in the feed, were also prepared. The results are presented in Table 1.

Physicochemical Measurements

The NMR spectra were recorded on a FT NMR Bruker Avance 300 instrument. Elemental analysis data were obtained by using a Leco CHNS-932 automatic analyzer. Molecular weight, based on calibration with monodispersed polystyrene standards, (Polymer Laboratories), were determined by GPC (Varian HPGPC, Model 8500) using a set of PL-gel columns with THF as solvent at room temperature. Differential scanning calorimetry was carried out on a Perkin-Elmer Diamond DSC with a scanning rate of 40°C/min in nitrogen and a sample size of 15 mg. Glass transition temperature was taken as the inflection point of the heat capacity discontinuity in the first scan. Thermogravimetric measurements were made with a Perkin-Elmer Pyris 6 TGA at a heating rate of 10°C/min under nitrogen.

Table 1

Polymerization conditions and properties of copolymers of MA-DiPrU with St; 2 wt% Bz_2O_2 in butanone at 70°C

Molar fraction of MA-DiPrU								
in feed	in copolymer[a]	Time (hrs)	Yield (g)	Conv. (%)	N (%)	T_g (°C)	$M_w \cdot 10^{-3}$ ($g\,mol^{-1}$)	$M_n \cdot 10^{-3}$ ($g\,mol^{-1}$)
0.2	0.085	7	0.0819	16.3	1.11	103	12.0	7.5
0.3	0.152	17	0.1524	23.0	2.01	107	11.3	7.3
0.4	0.208	21	0.1399	23.8	2.74	111	10.3	6.9
0.5	0.298	26	0.1169	18.5	3.93	113	10.7	7.6
0.6	0.387	50	0.0354	5.2	5.11	132	11.7	8.7
0.7	0.545	96	0.0455	6.3	7.20	141	9.6	6.2
0.8	—	96	traces	—	—	—	—	—
1.0	—	120	—	—	—	—	—	—

[a] Based on nitrogen content.

Results and Discussion

The results obtained by free-radical polymerization of MA-DiPrU with St of different comonomer mixture composition in the presence of 2 wt% Bz_2O_2 in 2 mL of butanone at 70°C are summarized in Table 1. It is evident that the copolymer yield depends on the molar ratios of comonomers in the feed, as well as on the polymerization time. Thus, for example, for the comonomers mixture of 0.2/0.8 molar fraction of MA-DiPrU/St after 7 h, the conversion of 16% was obtained, while for the comonomer mixture of 0.7/0.3 molar fraction of MA-DiPrU/St after 96 h, the conversion of 6.3% was reached. It should be also noted that MA-DiPrU does not polymerize under the free-radical polymerization conditions described in Table 1 even after 5 days of polymerization.

The data in Table 1 and Figure 1 show that the content of MA-DiPrU in copolymers is always lower than the content of St.

By assuming that MA-DiPrU does not homopolymerize and that the reactivity ratio in the copolymerization with St is equal, $r_1' = 0$, the reactivity ratio of St (r_2') can be calculated by equation (1), as previously proposed (7–9).

$$y' - 1 = r_1' x' \tag{1}$$

y' denotes the ratio of mole fractions of St to MA-DiPrU in the copolymers and x' is the ratio of the two monomers in the feed. The value for $r_2' = 1.70$ was calculated by using a linear-squares procedure from the plot of $y' - 1$ against x' in Figure 2 as the slope of the straight line.

From the data presented in Figure 1 for the copolymerization of MA-DiPrU with St of different comonomer compositions, the reactivity ratios, r_1 = MA-DiPrU and r_2 = St, are determined graphically by using the Kelen-Tüdös Equation (2) (Figure 3).

$$\eta = r_1 \xi - \frac{r_2}{\alpha(1 - \xi)} \tag{2}$$

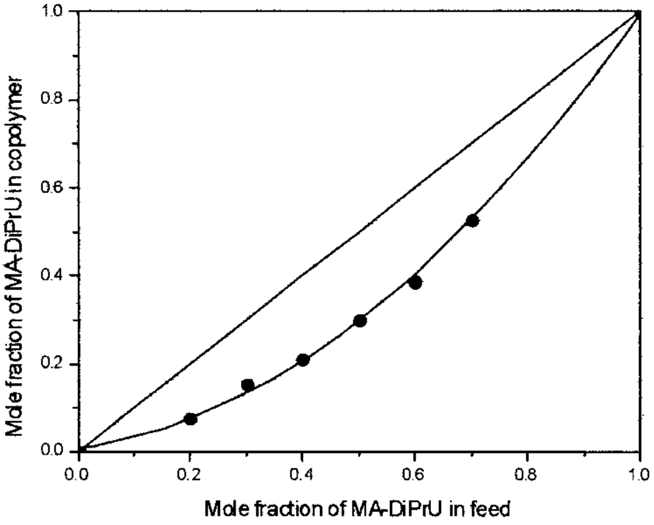


Figure 1. Ratio of molar fraction of MA-DiPrU in the feed and in the copolymer.

where η and ξ are functions of the molar fraction of monomers in the copolymers and in the feed, respectively and α is an arbitrary parameter (10). The reactivity ratios determined from Figure 3 are r_1 (MA-DiPrU) = 0.39; r_2 (St) = 1.03. The obtained data indicate a tendency of the monomers to alternating structure.

Molecular weights of all copolymers are approximately of the same values, M_w, 12,000–9600 and M_n, 8700–6200. From the data in Table 1, the initial rate of copolymerization was also calculated (Figure 4). It is evident that R_p decreases with increasing the content of MA-DiPrU monomer in the feed.

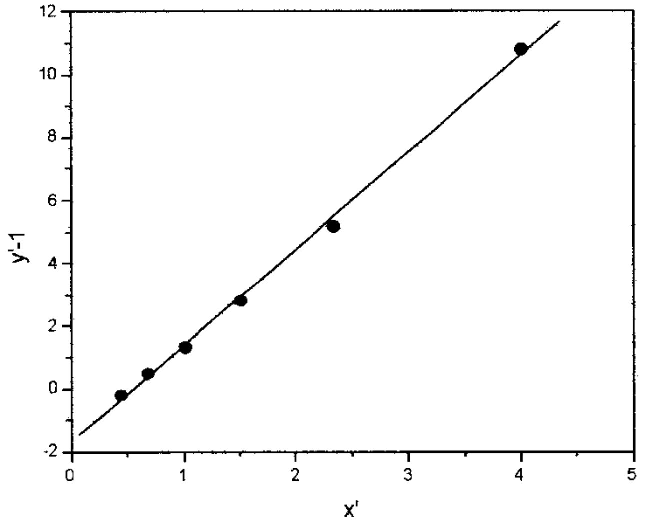


Figure 2. Plot of (y′−1) vs. x′ in copolymerization of St with MA-DiPrU in butanone at 70°C; 2% Bz_2O_2; (y′−1) is molar fraction of St/MA-DiPrU in copolymer and x′ in feed.

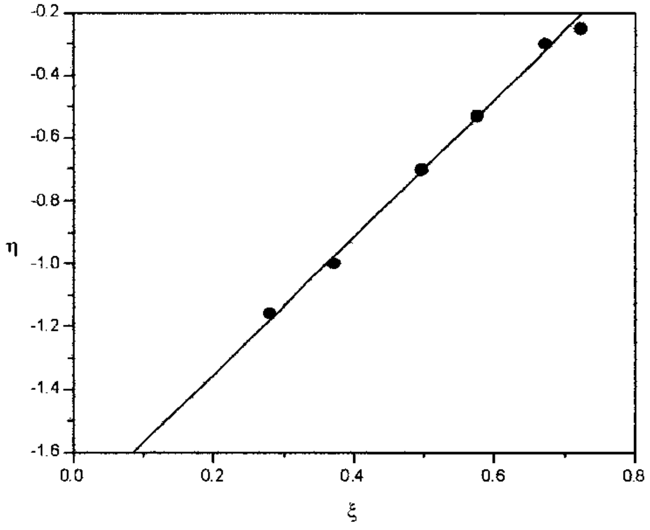


Figure 3. Kelen-Tüdös diagram for calculation of reactivity ratios in the copolymerization of MA-DiPrU with St.

Thermal Properties and Mechanism of Decomposition of Poly(MA-DiPrU-co-St)

Glass transition temperature in the copolymers MA-DiPrU with St increases with the increase of MA-DiPrU content in copolymers (Table 1 and Figure 5). Thermal analysis of poly(MA-DiPrU-co-St) shows that these copolymers are thermally stable materials which decompose between 180°C and 450°C by a two-step mechanism (Figure 6). In the first step, in the temperature range between 180°C and 250°C, a volatile fraction

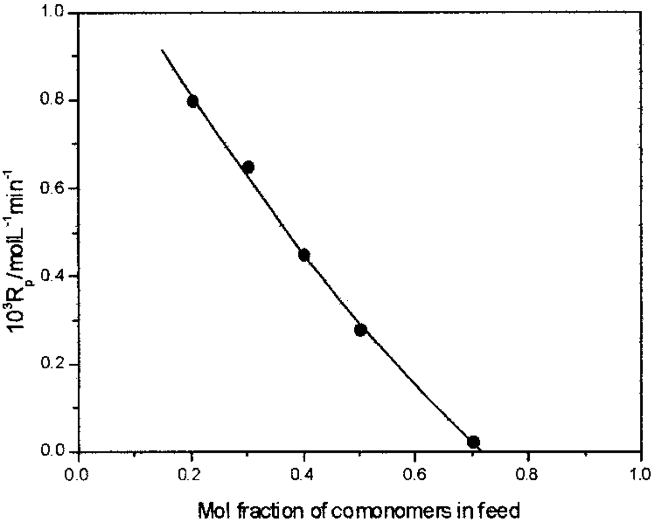


Figure 4. Initial rates of copolymerization of MA-DiPrU, with St vs. molar fraction of monomers in feed.

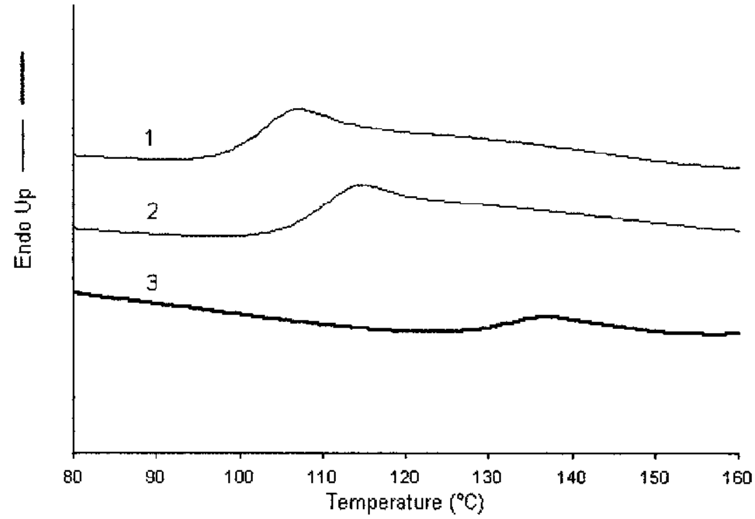


Figure 5. DSC tracings of poly(MA-DiPrU-co-St) with molar monomer ratios in copolymers MA-DiPrU: St = 1) 0.085: 0.915; 2) 0.208: 0.792; 3) 0.387: 0.613.

identified by NMR analysis as isopropylisocyanate (iPrNCO) separates. The residue, stable up to 280°C decomposes by a one-step mechanism in the temperature range of 280°C to 450°C without residue, was identified as copolymer of methacryl-isopropyl-amide (MA-iPrA) with St of different copolymer compositions.

From these results, it can be concluded that the decomposition of copolymers of MA-DiPrU with St proceeds as follows (Scheme 1).

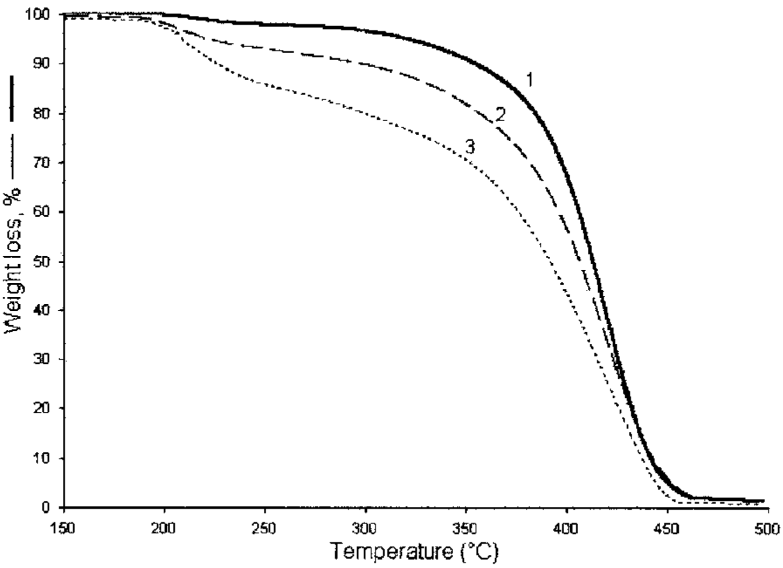
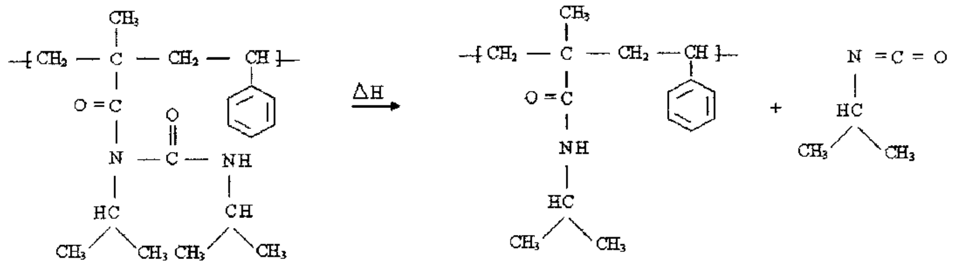


Figure 6. Thermograms of decomposition of poly(MA-DiPrU-co-St) with molar monomer ratios in copolymers MA-DiPrU: St = 1) 0.085: 0.915; 2) 0.208: 0.792; 3) 0.387: 0.613.



Scheme 1. Decomposition of poly(MA-DiPrU-co-St).

In order to prove the proposed mechanism of the decomposition of poly(MA-DiPrU-co-St) based on thermogravimetric analysis, thermal degradation experiments were performed by heating copolymers of different composition in TGA instrument in a nitrogen stream. The result obtained for the copolymer containing a 0.5 molar fraction of MA-DiPrU in feed (0.298 molar fraction in copolymer), copolymer 1, is presented in Figure 7. The experiment consisted of heating 16.5 mg of the copolymer 1 for 5 min at 250°C in nitrogen in a TGA analyzer, yielding 15.04 mg (90.65%) of poly(MA-iPrA-co-St), copolymer 2, as proved by ^{1}HNMR spectra.

Analysis of the copolymer 2: C, 83.71%; H, 8.17%; N, 2.84%. On the nitrogen content basis, copolymer 2 contains a 0.258 molar fraction of MA-iPrA. Volatile fraction was identified as isopropylisocyanate (iPrNCO). The yield of the volatile fraction calculated from the loss of weight in TGA analysis of sample 1 from Figure 7 is 11.4%. The theoretical amount iPrNCO in copolymer 1 is 10.6%, which corresponds to the experimental value.

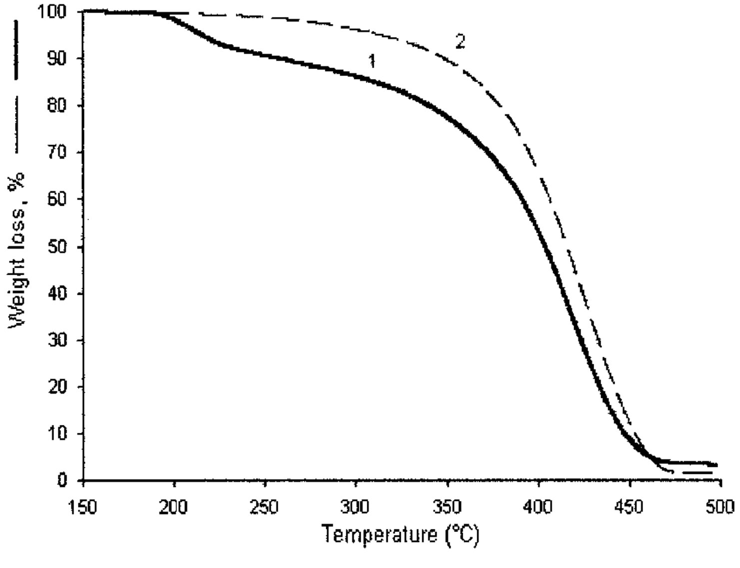


Figure 7. Thermograms of: 1) poly(MA-DiPrU-co-St), containing 0.298 molar fraction of MA-DiPrU; 2) poly(MA-iPrA-co-St), residue obtained after removal of iPrNCO by heating copolymer 1.

Conclusions

MA-DiPrU can copolymerize with St only after a long heating of comonomers at 70°C (from 7 to 96 h, depending on comonomer composition), by using 2 wt% of Bz_2O_2 in butanone as solvent.

Copolymerization of MA-DiPrU with St is a statistical reaction in which, regardless of monomer-to-monomer ratios in the feed, an excess of St was in the copolymers. Molecular weights of copolymers are approximately of the same values ($M_w \sim 11000$ and $M_n \sim 7000$).

All copolymers decompose under TGA conditions by a two-step mechanism. In the first step, at a temperature between 180°C and 250°C in nitrogen separates isopropylisocyanate (iPrNCO) under the formation of thermally stable poly (MA-iPrA-co-St). Glass transition temperature of all copolymers is within the thermally stable region.

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