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SYNTHESIS AND POLYMERIZATION OF N-ACRYL-DICYCLOHEXYLUREA AND N-METHACRYL-DICYCLOHEXYLUREA AND COPOLYMERIZATION WITH α -METHYLSTYRENE

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SYNTHESIS AND POLYMERIZATION OF N-ACRYL-DICYCLOHEXYLUREA AND N-METHACRYL-DICYCLOHEXYLUREA AND COPOLYMERIZATION WITH α -METHYLSTYRENE

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Key Words: Acryl-dicyclohexylurea, Metacryl-dicyclohexylurea, Poly(acryl-dicyclohexylurea), Poly(acryl-dicyclohexylurea-co- α MeSt), Poly(cyclohexylacrylamide), Poly(cyclohexylacrylamide-co- α MeSt), Reactivity Ratios, Rate of Copolymerization, Mechanism of Thermal Degradation of Polymers and Copolymers

ABSTRACT

The title compounds have been prepared by the addition of acrylic acid and methacrylic acid to dicyclohexylcarbodiimide (DCC). N-Acryl-N,N'-dicyclohexylurea (Acryl-DCU) homo-polymerizes and copolymerizes with α -methylstyrene (α MeSt), while Methacryl-DCU does not polymerize under the standard free-radical-initiated polymerization. Copolymers of Acryl-DCU with α MeSt prepared under different monomer-to-monomer ratios in the feed have random composition with an azeotropic point at ratio of 0.75 (Acryl-DCU) to 0.25 (α MeSt). Reactivity ratios determined by the Kelen-Tüdös method are r_1 (Acryl-DCU) =

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0.72 and r_2 (α MeSt) = 0.07. Poly(Acryl-DCU) and copolymers with α MeSt decompose under the TGA conditions by a two step mechanism. In the first step between 180 and 250°C, cyclohexylisocyanate separates by degradation of dicyclohexylurea in the side chain, while the thermally stable residue represents the poly(cyclohexylacrylamide) and copolymers with α MeSt.

INTRODUCTION

During the last few decades a large number of comb-like polymers and copolymers which contain mesogenic groups in side chains were prepared. The interest in studies of these polymers stems from the fact that many of these polymers show a tendency to smectic ordering in the amorphous polymer matrix [1-5]. In the present paper, we shall describe the synthesis and polymerization of N-acryl-, and N-methacryl dicyclohexylurea monomers.

As far as we know, polymers and copolymers which contain dicyclohexylurea as a pending group have not been prepared so far. Monomers Acryl-DCU and Methacryl-DCU were prepared by the addition of DCC with acrylic and methacrylic acid, respectively. The addition of carboxylic acids to DCC proceeded at room temperature in THF as solvent, but in all cases, a part of dicyclohexylurea (DCU) separated, thus indicating that a part of carboxylic acid was converted to acid anhydride. It is of interest to note that following the procedure described in the Experimental section, Acryl-DCU could not be isolated without the addition of polymerization inhibitor, which was not the case in the preparation of Methacryl-DCU. It has been further found that Acryl-DCU readily homopolymerizes and copolymerizes with α -methylstyrene (α MeSt) in the presence of benzoylperoxide, while Methacryl-DCU does not polymerize nor copolymerize under the same conditions.

EXPERIMENTAL

Monomers

N-Acryl-N,N'-dicyclohexylurea (Acryl-DCU)

To a solution of 8.24 g (0.04 mole) of DCC in 50 mL of THF there were added, with stirring at room temperature, 2.84 mL (0.04 mole) of acrylic acid and 0.2 g of hydroquinone in 20 mL THF. After a few minutes, a shining crystalline product slowly separated. The reaction mixture was left overnight at room tem-

perature, the crystalline product was separated by filtration and washed with a few milliliters of THF. The yield of DCU was 2.64 g (29.4% calculated on the basis of DCC); m.p. 233-234°C (under the sublimation at 180°C); lit. m.p. of commercial DCU was 232-233°C. The mother liquor after the removal of DCU was evaporated in the vacuum without heating to a total of 15 g, and the residue was treated with 50 mL of petrol ether (b.p. 40-60°C). The white crystalline product was filtered off, yielding 4.6 g (41.4% based on DCC) of Acryl-DCU; m.p. 137-138°C.

Analysis: Calcd. for $C_{16}H_{26}N_2O_2$ (%): C, 69.00; H, 9.41; N, 10.06. Found: C, 69.16; H, 9.39; N, 10.11.

N-Methacryl-N,N'-dicyclohexylurea (Methacryl-DCU)

Methacrylic acid (3.38 mL, 0.04 mol) and 8.24 g (0.04 mol) of DCC were dissolved in 50 mL THF and after standing overnight at room temperature, 3.5 g of DCU (39% based on DCC) was filtered off, THF from the mother liquor was evaporated to dryness in vacuum, and the residue (8.8 g) was dissolved in 8 mL of chloroform under the addition of 100 mL of petroleum ether (b.p. 40-60°C). After standing overnight in a refrigerator, the white crystalline product was filtered off, yielding 4.0 g (34%) of Methacryl-DCU, melting at 148-149°C.

Analysis: Calcd. for $C_{17}H_{28}N_2O_2$ (%): C, 69.83; H, 9.65; N, 9.58. Found: C, 69.52; H, 9.22; N, 9.57.

Polymerization Procedure

Polymerization of Acryl-DCU and Methacryl-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 with α MeSt were initiated with 1 wt% of dibenzoylperoxide in butanone as solvent. The solution of polymers was diluted with chloroform and precipitated by a drop-wise addition of methanol. The polymer was filtered off and dried in vacuum at 80°C overnight. Composition of copolymers was determined from the nitrogen content and from the 1H NMR spectra (Table 1).

Physicochemical Measurements

1H NMR spectra were obtained on a Varian EM 390 spectrometer. The copolymer composition was determined by 1H 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 jump. The thermo-

TABLE 1. Polymerization Conditions and Properties of Poly(Acryl-DCU) and Copolymers with α MeSt; 1 wt% Bz₂O₂ in Butanone at 70°C

Molar fraction of Acryl-DCU in feed	Molar fraction of Acryl-DCU in copolymer		Butanone (mL)	Time (hr)	Yield (g)	Conv. (%)	N (%)	$M_w \cdot 10^{-3}$ $M_n \cdot 10^{-3}$	
	a)	b)						(g mol ⁻¹)	
0.1	0.37	0.37	1	96	0.076	5.68	5.81	8.5	5.7
0.2	0.48	0.49	2	72	0.052	8.37	6.91	10.2	6.6
0.3	0.53	0.53	2	50	0.094	14.22	7.31	9.5	6.2
0.4	0.57	0.59	1.5	48	0.162	29.66	7.76	15.4	8.5
0.5	0.62	0.62	1	48	0.209	53	7.98	22.7	11.3
0.6	0.67	0.70	1	45	0.253	59.15	8.34	29.9	13.5
0.7	0.74	0.74	1	44	0.323	70.67	8.74	29.9	13.6
0.8	0.77	0.80	0.7	44	0.301	82.23	8.98	29.4	15.4
0.9	0.84	0.83	0.7	7	0.098	62.96	9.30	30.2	13.5
1.0	1.00	-	1.5	20	0.175	87.20	9.97	30.0	14.0

a) based on nitrogen content; b) based on ¹H NMR data

gravimetric 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 styrogel columns with THF as solvent at room temperature.

RESULTS AND DISCUSSION

Free-Radical-Initiated Polymerization of Acryl-DCU and Copolymerization with α MeSt

Polymerization conditions and properties of poly-Acryl-DCU and poly(Acryl-DCU-co- α MeSt) are presented in Table 1 and in Figure 1. The copolymer composition is determined from the nitrogen content and from the ¹H NMR spectra in deuterated chloroform.

The data in Table 1 and in Figure 1 indicate that the copolymerization of Acryl-DCU with α MeSt is a statistical reaction with an azeotropic point at ratio of 0.75 (Acryl-DCU) to 0.25 (α MeSt). The initial rate of copolymerization shown in Figure 2 indicates that the rate increases almost linearly with the increase of Acryl-DCU in the monomer feed.

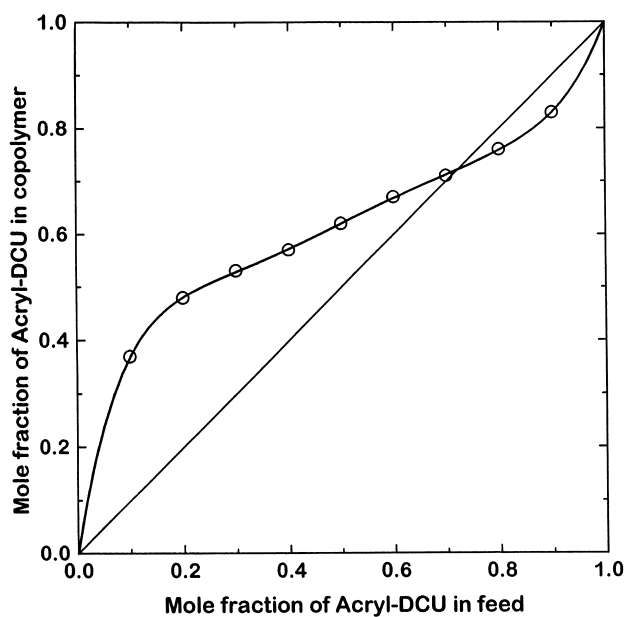


Figure 1. Ratio of molar fraction of Acryl-DCU in feed and in copolymer with α MeSt.

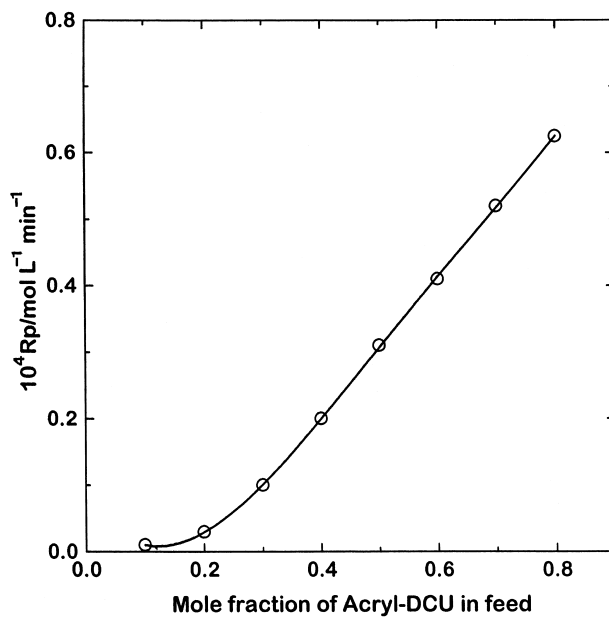


Figure 2. Initial rate of copolymerization against molar concentration of Acryl-DCU in copolymerization with α MeSt in butanone at 70°C ; 1 wt% of Bz_2O_2 .

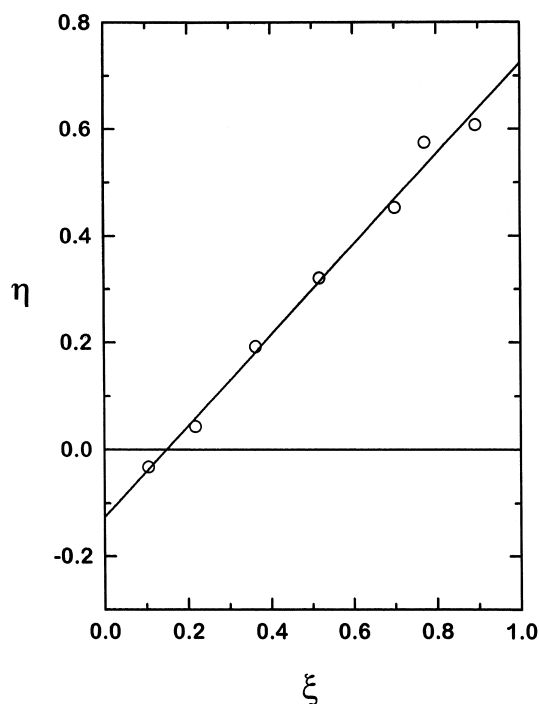


Figure 3. Kelen-Tüdös diagram for calculation of r_1 (Acryl-DCU) = 0.72 and r_2 (α MeSt) = 0.07.

The reactivity ratios in copolymerization have been determined by the Kelen-Tüdös Equation 1 (Figure 3):

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

where η and ξ are functions of the molar fractions of monomer in the copolymer and in the feed respectively, and α is an arbitrary parameter [6]. Numerical values of the reactivity ratios determined from the Figure 3 using the least square method are r_1 (Acryl-DCU) = 0.72 and r_2 (α MeSt) = 0.07.

Thermal Stability and Mechanism of Decomposition of Poly(Acryl-DCU) and Copolymers with (α MeSt)

Poly(Acryl-DCU) and copolymers with α MeSt are thermally stable, film forming materials which decompose in TGA experiments between 180°C to 450°C by the two step mechanism. As shown in Figure 4, weight loss in the first

step is 43% between 150°C and 250°C. The residue is stable up to a temperature of 300°C, and then it decomposes by the one-step mechanism up to 450°C without a residue.

As shown in Figure 4, the residue after removal of 43% of the volatile fraction represents a thermally stable part of the repeating units in the polymer chain. The subsequent analysis of the volatile fraction and the residue indicates that poly(Acryl-DCU) decomposes in the manner shown in Scheme 1 under the formation of poly(cyclohexylacrylamide) and cyclohexylisocyanate.

In order to prove the proposed mechanism of decomposition of poly(Acryl-DCU) based on the thermogravimetric analysis, a preparative decomposition of homopolymer was performed. A sample of 0.2 g of poly(Acryl-DCU) was heated for 20 minutes in vacuum of 0.26 kPa (2 mm Hg) at 220°C, and both liquid volatile fraction and solid residue were collected and analyzed without further purification.

Analysis of the volatile fraction: Calcd. for cyclohexylisocyanate, $C_7H_{11}NO$ (%): C, 67.21; H, 8.80; N, 11.20. Found: C, 67.28; H, 8.74; N, 11.04. The IR spectra of the volatile fraction were identical to the spectra of the original sample of cyclohexylisocyanate.

Analysis of the solid residue: Calcd. for poly(cyclohexylacryl-amide), $C_9H_{15}NO$ (%): C, 70.55; H, 9.87; N, 9.14. Found: C, 69.31; H, 9.28; N, 8.81. The

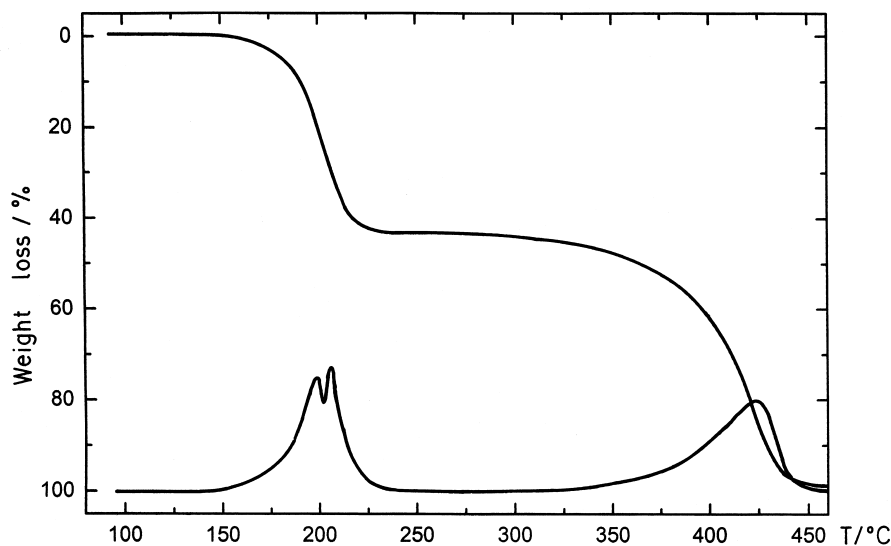
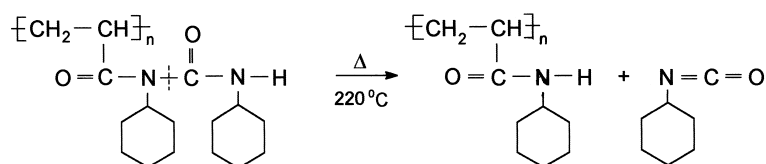


Figure 4. Thermogravimetric analysis of poly(Acryl-DCU) in nitrogen; heating rate $10^\circ\text{C min}^{-1}$.



Scheme 1. Thermal decomposition of poly(Acryl-DCU)

proposed structure of the residue was confirmed by ^1H NMR spectrum (Figure 5) which showed the resonance signal values at 0.5–3.0 ppm (–CH; CH_2); 3.4–4.0 ppm (CH–N–); 5.5–7.0 ppm (–NH).

Plots of TGA curves of poly(Acryl-DCU) and poly(Acryl-DCU-co- α MeSt) with different monomer-to-monomer ratios in copolymers are shown in Figure 6.

As evident from the Figure 6, polymers of Acryl-DCU with α MeSt decompose under the same two-step mechanism as previously shown for the decomposition of poly(Acryl-DCU). A detailed analysis of the volatile product and the residue was performed for copolymer 2 (Figure 6) with the molar ratio of Acryl-DCU: α MeSt = 0.62: 0.38. A sample of copolymer 2 (0.2 g) was decomposed in vacuum at 220°C under the same conditions as described for homopolymer 1. The yield of volatile fraction was 34% corresponding to the value of weight loss in the first step of copolymer 2 in Figure 6.

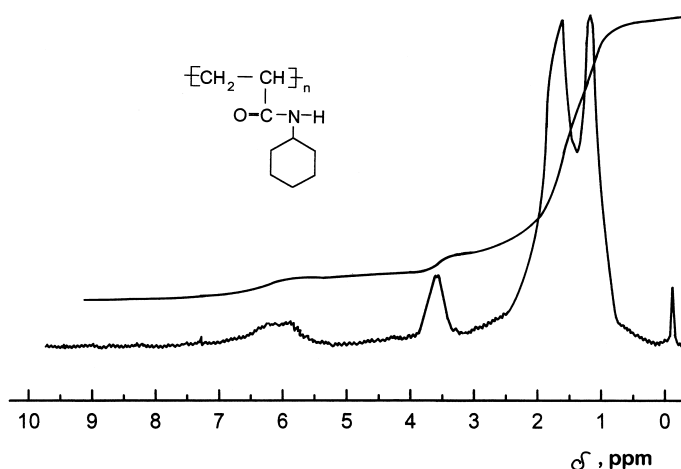


Figure 5. ^1H NMR spectrum of poly(cyclohexylacrylamide) (solid residue of the thermal decomposition of poly(Acryl-DCU)).

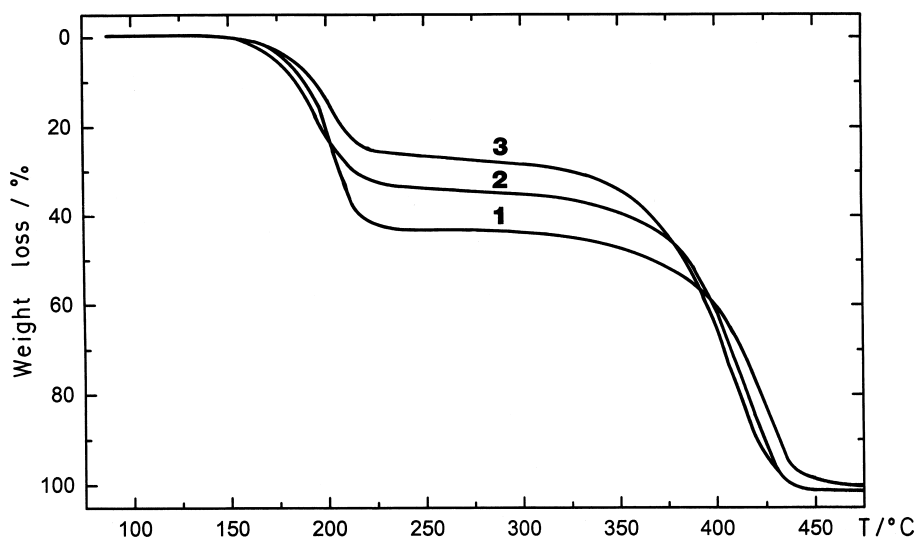


Figure 6. Thermograms of decomposition of poly(Acryl-DCU) (1) and poly(Acryl-DCU-co- α MeSt) with molar monomer ratios in copolymers: Acryl-DCU: α MeSt = 0.62: 0.38 (2); Acryl-DCU: α MeSt = 0.48: 0.52 (3) in N_2 ; heating rate $10^\circ C \text{ min}^{-1}$.

Analysis of the volatile fraction: Calcd. for $C_7H_{11}NO$ (cyclo-hexylisocyanate) (%): Found: C, 67.51; H, 9.04; N, 10.92. 1H NMR and IR spectra are identical to the commercial sample of cyclohexylisocyanate.

Analysis of the crude residue of copolymer decomposition without purification: Calcd. for (cyclohexylacrylamide): α MeSt = 0.62 : 0.38 (%): N, 6.21; Found: N, 6.25.

1H NMR spectrum (Figure 7) shows the resonance signals values at 0.3-3.0 ppm (CH_2 groups of cyclohexyl and α MeSt; CH_3 of α MeSt); 3.0-4.0 ppm ($CH-N$ from cyclohexylacrylamide); 4.0-6.5 ppm (NH groups); 6.5-7.7 ppm (resonance signals for $-CH-$ of phenyl ring). The resonance signals of 1H NMR in Figure 7 correspond to the 1H NMR spectrum of copolymer of N-cyclo-hexylacrylamide with α MeSt prepared by Pazhanisamy and co-workers [7].

Based on the nitrogen content and resonance signal values of 1H NMR spectrum of the thermostable residue of the poly(Acryl-DCU-co- α MeSt), it has been proved that the residue consisted of poly(cyclohexylacrylamide-co- α MeSt).

Glass transition temperatures and weight losses at temperatures close to T_g 's for poly(Acryl-DCU) and copolymers which contain different molar ratios of Acryl-DCU to α MeSt are presented in Table 2. Prior to the T_g determination, all

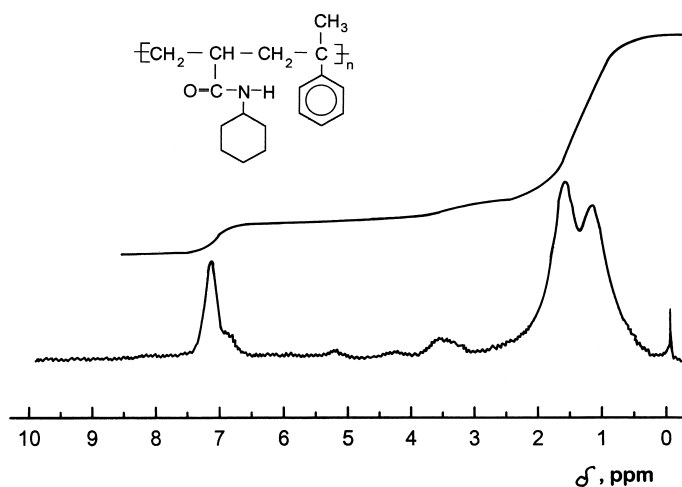


Figure 7. ^1H NMR spectrum of poly(cyclohexylacrylamide-co- αMeSt) (solid residue of thermal decomposition of copolymer Acryl-DCU-co- αMeSt ; molar ratio of monomers 0.62 to 0.38).

samples had been predried at 140°C in the DSC furnace in order to remove traces of absorbed water or solvent. After that, samples were quenched to ambient temperature as rapidly as possible in the instrument and then scanned at $40^\circ\text{C min}^{-1}$ (first scan) The second scan was carried out by reheating the sample under the same conditions after cooling to 50°C . Since the T_g values of homo-polymer and copolymers are close to their degradation temperatures, weight loss at the temperatures corresponding to the T_g 's are also presented in Table 2.

Evidently, T_g 's obtained in the first scan have changed from 160 to 190°C , depending on the copolymer composition. T_g 's are higher for the copolymer with higher Acryl-DCU content. In the second scan the T_g 's are significantly decreased, probably due to the presence of small amount of volatile cyclohexylisocyanate. Similar to the T_g 's of copolymers of Acryl-DCU with αMeSt , the T_g 's of residues are increased when the content of cyclohexyl-acrylamide in copolymer increases (Table 2).

Figure 8 illustrates the typical DSC curves of the first scan (1) and second scan (2) of the copolymer which contains the molar ratio of Acryl-DCU: αMeSt = 0.62: 0.38 and the DSC curve (3) of the thermally stable residue of the same copolymer after heating at 220°C .

TABLE 2. Glass Transition Temperature and Weight Loss of Poly(Acryl-DCU) and Copolymers with α MeS

Molar fraction of Acryl-DCU in copolymer ^a	T _g /°C, at heating rate 40°C min ⁻¹		Weight loss/% at:				
	First scan	Second scan	Residue	160°C	170°C	180°C	190°C
0.37	160	132		1.3	3.5	6.5	9.0
0.48	163	132		1.1	3.0	6.0	8.5
0.53	168	134	155	1.1	3.0	6.0	9.5
0.57	173	134		1.1	3.0	6.0	9.5
0.62	174	133	159	1.0	2.5	5.0	9.0
0.67	177	134		1.0	2.3	5.0	9.0
0.74	178	135	160	0.8	2.0	4.8	8.5
0.77	180	138		0.8	1.9	4.0	8.0
0.84	181	138		0.8	1.9	4.0	8.0
1.00	184	138	161	0.8	1.4	3.8	7.0

^a based on nitrogen content

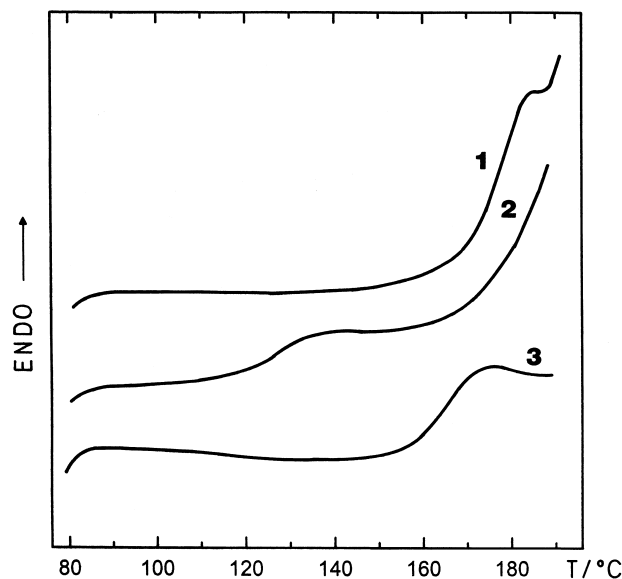


Figure 8. DSC tracings of 1) first scan and 2) second scan of poly(Acryl-DCU-co- α MeSt) with comonomer ratio of 0.62: 0.38; 3) DSC tracing of poly(cyclohexylacrylamide-co- α MeSt) of the comonomer ratio 0.62: 0.38.

CONCLUSION

Monomers acryl-dicyclohexylurea (Acryl-DCU) and Methacryl-DCU were prepared by the addition of acrylic acid and methacrylic acid to dicyclohexylcarbodiimide.

Acryl-DCU readily homopolymerized and copolymerized with α MeSt in the presence of dibenzoylperoxide, while Methacryl-DCU did not polymerize under the same conditions.

Homopolymerization and copolymerization of Acryl-DCU were performed in butanone, yielding a statistical copolymer with an azeotropic point at a molar ratio of 0.75 (Acryl-DCU) to 0.25 (α MeSt).

Molecular weights of copolymers increased from $8.5 \times 10^3 \text{ g mol}^{-1}$ to $30 \times 10^3 \text{ g mol}^{-1}$ when molar ratio of acrylic acid to α MeSt in the feed increased from 0.1 to 0.9. M_w of homopolymer was $30 \times 10^3 \text{ g mol}^{-1}$.

Poly(Acryl-DCU) and copolymers with α MeSt decomposed by the two-step mechanism. Under the TGA conditions in the first step, a quantitative yield of cyclohexylisocyanate separated by a decomposition of dicyclohexylurea. The thermally stable residue represented poly(cyclohexylacrylamide), and copoly-

mer with α MeSt. T_g of poly(Acryl-DCU) was at 184°C, and of the residue after the removal of dicyclohexylisocyanate T_g was at 161°C. Copolymer with molar ratio of Acryl-DCU: α MeSt = 0.62: 0.38 had T_g at 174°C, and of the residue T_g was at 159°C.

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