Polymer Bulletin 11, 505–510 (1984)

Polymer Bulletin

Reactions

Functional Polymers

36.* N-Acryl(Methacryl)N,N'-Dicyclohexylurea: Monomers and Polymers

Shoukuan Fu, Shanjun Li and Otto Vogl**

Polytechnic Institute of New York, Brooklyn, New York 11201, USA

ABSTRACT

N-Acryl-N,N'-dicyclohexylurea and N-methacryl-N,N'-dicyclohexylurea have been synthesized. N-Acryl-N,N'-dicyclohexylurea was polymerized with azobisisobutyronitrile as the initiator and the copolymerization of these two monomers with styrene and methyl methacrylate was also accomplished. Monomers, polymers, and copolymers were characterized.

INTRODUCTION

The reaction of N,N'-dicyclohexylcarbodiimide with carboxylic acids has been studied extensively in recent years (1,2). It is initiated by the addition of the proton to the nitrogen atom of the carbodiimide followed by the addition of the acylate anion to the central carbon atom. RN=C(NHR)-OCOR' can rearrange to N-acyl urea, or carbodiimide and the carboxylic acid can form N,N'-dicyclohexylurea and the acyl anhydride which in turn can acylate N,N'-dicyclohexylurea to N-acyl-N,N'-dicyclohexylurea. The product of the reaction depends on the nature of the carbodiimide, the acid, the solvent, and the temperature (1,2).

We studied various methods for the preparation of acrylates and methacrylates of 2(2-hydroxyphenyl)2H-benzotriazoles, especially under mild conditions. With certain phenols we succeeded in synthesizing the desired acrylates or methacrylates (3,4). In other cases, acrylic acid (AA) or methacrylic acid (MA) and N,N'-dicyclohexylcarbodiimide (DCI) were consumed, but none of the desired acrylate or methacrylate was obtained. Rather, compounds of m.p. 136° C and m.p. 146° C, respectively, were produced. It appeared that N-acryl-N,N'-dicyclohexylurea (ADCU) and N-methacryl-N,N'-dicyclohexylurea (MDCU) had been formed during this reaction. MDCU, m.p. 145° C, has been reported previously as a by-product of the reaction of DCI with α-methylthioglycidic acid followed by treatment with ammonia.

It was our objective to prepare ADCU and MDCU, to characterize the two monomers, and to attempt and study briefly their polymerization.

EXPERIMENTAL PART

A. Materials

Acrylic acid (AA), methacrylic acid (MA), 4-pyrrolidinopyridine (4-PP), dicyclohexylcarbodiimide (DCI) and magnesium sulfate (Aldrich

---

* Part XXXV: O. Vogl, Polimery, in press.

**To whom all communications should be addressed.

Chemical Co.) were used as received. Tetrahydrofuran (Aldrich Chemical Co.) (THF) was heated to reflux with lithium aluminum hydride (Alpha Products) and distilled under a nitrogen atmosphere before use. Styrene (St) and methyl methacrylate (MMA) (Aldrich Chemical Co.) were distilled before use.

Azobisisobutyronitrile (AIBN) (Aldrich Chemical Co.) was recrystallized three times from absolute methanol and dried for one day at 0.05 mm Hg at room temperature.

Solvents such as benzene, acetic acid, dichloromethane (DCM), chloroform, N,N'-dimethylacetamide (DMAc), and ethanol were used without distillation.

B. Procedures

1. Monomer Preparations:

a. 1-N-Methacryl-N,N'-dicyclohexylurea (MDCU): Into a 250 mL round-bottom flask equipped with a magnetic stirrer was placed DCI (2.27 g, 11 mmol), MA (0.86 g, 10 mmol), and 4-PP (0.15 g, 1 mmol) in THF (100 mL); the mixture was stirred at room temperature for 2 hr, followed by the addition of benzene (50 mL). The N,N'-dicyclohexylurea (DCU) which had precipitated was filtered, the filtrate was washed with water (3 x 50 mL), 5% acetic acid solution (3 x 50 mL), and again with water (3 x 50 mL), dried over magnesium sulfate overnight, and the solvent was evaporated on a rotary evaporator. A yield of 1.2 g (41%) of MDCU was obtained; MDCU was recrystallized from n-hexane; white needles, m.p. 145-146°C were obtained. IR (KBr): 1680 cm^{-1} ($\nu_{C=O}$ stretching).

The ^1H and ^{13}C NMR chemical shift data are presented in Table 1.

Anal. Calcd. for $C_{17}H_{28}N_2O_2$: C, 69.83%; H, 9.65%; N, 9.58%. Found: C, 69.46%; H, 9.78%; N, 9.62%.

b. N-Acryl-N,N'-dicyclohexylurea (ADCU): The synthesis of ADCU followed essentially the same procedure as described for the synthesis of MDCU, except that AA (0.72 g, 10 mmol) was used instead of MA. The crude product (1.5 g, 54% yield) was recrystallized from n-hexane and gave ADCU as white needles, m.p. 136-137°C. IR (KBr): 1680 cm^{-1} ($\nu_{C=O}$ stretching).

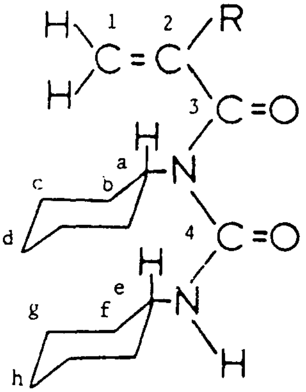
The ^1H and ^{13}C NMR chemical shift data are presented in Table 1.

Anal. Calcd. for $C_{16}H_{26}N_2O_2$: C, 69.03%; H, 9.41%; N, 10.06%. Found: C, 69.03%; H, 9.68%; N, 10.06%.

2. Polymerizations

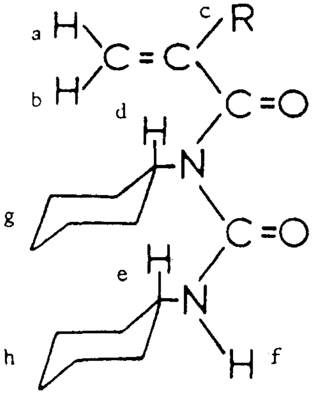
a. Homopolymerizations of N-Acryl-N,N'-dicyclohexylurea (ADCU): A 10 mL polymerization tube was charged with 2 mmol of ADCU (0.56 g), DCM (2.5 mL), and AIBN (1.0 mg, 0.3 mol %). After three freeze-thaw cycles at 0.05 mm Hg pressure to degas the homogeneous solution, the tube was sealed and allowed to react for 3 days at 50°C. Then the tube was opened, the solution was diluted with DCM (2.5 mL) and poured into methanol (200 mL). The polymer precipitated, the suspension was filtered and dried at 0.1 mm Hg, dissolved in DCM (5 mL), and precipitated again into methanol (200 mL). After drying at 0.1 mm Hg, poly-ADCU was obtained in 90-95% yield (0.50-0.53 g).

TABLE 1



^{13}C-NMR Chemical Shift Values (ppm)[1]

	COMPOUND	
	ADCU	MDCU
1	129.8	115.7
2	128.6	142.0
3	166.3	173.9
4	153.8	154.1
R	-	20.0
a	56.1	58.2
b	30.8	30.8
c	26.3	26.5
d	25.5	25.6
e	50.0	49.6
f	32.7	32.7
g	24.7	24.7
h	25.4	25.3



^{1}H-NMR Chemical Shift Values (ppm)[1]

	COMPOUND	
	ADCU	MDCU
a	6.37 d	5.23 sh,m
b	6.45 d	5.15 sh,m
c	5.70 q	2.00 sh,s
d	4.02 m	3.91 m
e	3.70 b	3.67 b,m
f	7.14 b,d	7.29 b,m
g&h	0.80- 2.30 m	0.90- 2.40 m

s singlet

d doublet

q quartet

m multiplet

b broad

sh sharp

---

[1] TMS Standard (0 ppm)

The polymerization of MDCU was attempted in a similar way, but no polymer precipitated after the normal work-up. After evaporating the solvent, the monomer MDCU, m.p. 145° C, was recovered in nearly quantitative yield.

b. Copolymerization of N-Acryl(Methacryl)-N,N′-dicyclohexylurea with Styrene or Methyl Methacrylate: N-Acryl(Methacryl)-N,N′-dicyclohexylurea (ADCU or MDCU) were copolymerized with styrene (St) or methyl methacrylate (MMA), respectively. The procedure was essentially the same as that described for the homopolymerization. The amount of material used for the polymerizations and the results of all polymerizations including polymerization yield, polymer composition, and inherent viscosity of the polymers are presented in Table 2.

RESULTS AND DISCUSSION

ADCU and MDCU were synthesized in yields of about 65-70% from N,N′-dicyclohexylcarbodiimide (DCI) and AA or MA, respectively, with 4-PP as catalyst. Purification was readily accomplished by recrystallization from n-hexane, and the characterization was done by IR, ^{1}H, and ^{13}C NMR spectroscopy. ADCU and MDCU had first been isolated when we tried to esterify 2,2,6,6-tetramethyl-4-piperidinol with AA or MA in the presence of DCI. None of the expected esters of 2,2,6,6-tetramethyl-4-piperidinol were formed and ADCU or MDCU were the only products of the reactions. On the other hand, when the AA or MA were allowed to react with the phenolic hydroxyl groups of a benzotriazole derivative, for example 1,3(2,4-dihydroxyphenyl)-2H-dibenzotriazole, the phenol esters but no ADCU or MDCU were formed.

These observations are in agreement with the literature (2,6) which states that under neutral conditions of the esterification of carboxylic acids with alcohol or phenols in the presence of DCI the reaction favors the formation of the N-acylurea derivatives as by-products, but under acidic conditions the ester is formed exclusively. These generalizations are in agreement with our findings; as a consequence, for the actual synthesis of ADCU or MDCU, 4-PP was used as an effective catalyst of the reaction of AA or MA with DCI.

It was noted during the first isolation of ADCU when drying the compound at 100° C, that a substantial part of ADCU had polymerized, even in the solid state. It was then found that ADCU homopolymerized readily with AIBN as the initiator and also copolymerized well with such resonance stabilized monomer as St or MMA. In all cases, polymers were obtained in high yield and with good molecular weight (Table 2). ADCU was incorporated to 25 mol percent into the St copolymer and 16 mol percent into the MMA copolymer, at a monomer feed containing 20 mol percent of ADCU.

MDCU behaved quite differently as the monomer in attempted polymerizations. In spite of special purification of MDCU, no homopolymer could be obtained under a variety of polymerization conditions; the monomer was always recovered unchanged. We interpret this failure to obtain the homopolymer of MDCU as a result of the well-known ceiling temperature phenomena (methyl methacrylate has a ceiling temperature of polymerization of about 165° C in one molar solution, but the ceiling temperatures of acrylates are much higher) and do not believe that possible impurities in the monomer are responsible for the inhibition of the MDCU polymerization. In our cases the polymerizations were carried out in solution of about 20% concentrations of the monomer MDCU, which amounts to a molarity of about 0.6 molar. Copolymers of MDCU could be made with St or MMA, but even here

TABLE 2: Homopolymerization of ADCU and Copolymerization of ADCU and MDCU with Styrene or Methyl Methacrylate. Polymerization Conditions: Temperature: 50° C; Time: 3 days; Solvent: Dichloromethane, 2.5 mL; Initiator: AIBN, 0.3 mol percent; Sealed tube (pressure 0.05 mm Hg).

Monomers						Total amount of monomers		Polymerization yield		Polymer composition in mol-% ADCU (or MDCU) unit	η_{inh} [a)] DMAc (dL/g)
M_1			M_2								
Type	g	mmol	Type	g	mmol	g	mmol	g	%		
ADCU	0.56	2	--		--	0.56	2	0.53	95	100	0.53[b)]
ADCU	0.56	2	--		--	0.56	2	0.50	90	100	0.58[b)]
ADCU	0.42	1.5	St	0.62	6	1.04	7.5[c)]	0.82	79	25	0.28
ADCU	0.42	1.5	MMA	0.60	6	1.02	7.5[c)]	0.91	89	16	0.63
MDCU	0.59	2	--		--	0.59	2	d)		--	--
MDCU	0.59	2	--		--	0.59	2	d)		--	--
MDCU	0.44	1.5	St	0.62	6	1.06	7.5[c)]	0.26	25	4	0.29
MDCU	0.44	1.5	MMA	0.60	6	1.04	7.5[c)]	0.57	55	4	0.37

a) 0.5 g/dL in DMAc, 30° ± 0.1° C.
b) Chloroform was used as solvent.
c) Feed ratio of comonomer mixture was always 20 mol percent in M_1.
d) Only monomer was recovered, m.p. 145° C.

the polymer yields were lower and the incorporation of MDCU in the copolymers was only 4 mol percent at a monomer feed of 20 mol percent.

ACKNOWLEDGMENT

This work was supported by Grant No. 955531 from the Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, and in part by a grant from the National Science Foundation. We would like to express our appreciation to W. Bassett, Jr., for measuring and calculating the NMR spectra.

REFERENCES

1. H.G. Khorana, Chem. Rev. 53, 145 (1953).
2. F. Kurzer and K. Douraghi-Zadeh, Chem. Rev. 67(2), 107 (1967).
3. S.J. Li, A. Gupta, A.C. Albertsson and O. Vogl, in press.
4. S.J. Li, W. Bassett, Jr., F. Xi and O. Vogl, in press.
5. L.P. Parshina, M.G. Linkova, O.V. Kildisheva and I.L. Knunyants, Izv. Acad. Nauk SSR, Ser. Khim. (4), 931 (1970); CA 73, 35130b (1970).
6. K. Holmberg and B. Hansen, Acta Chim. Scand., Ser. B B33(6), 410 (1979).

Accepted May 9, 1984