Synthesis of Nanoporous Crosslinked Poly(Acryl-*N*-cyclohexyl Amide-co-Ethylene Glycol Dimethacrylate) by Thermal Degradation of Poly(Acryl-*N,N'*-dicyclohexylurea-co-Ethylene Glycol Dimethacrylate)

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ABSTRACT

Crosslinked unswellable copolymers of acryl-dicyclohexylurea (A-DCU) with ethylene glycol dimethacrylate (EDMA) at monomer-to-monomer ratios in the feed: 0.3/0.7; 0.5/0.5; 0.7/0.3; 0.8/0.2 were prepared by free radical copolymerization in butanone in the presence of 1% of benzoyl peroxide. The reaction was performed up to high conversion yielding 99–100% of copolymer. Copolymers regardless of the ratio of comonomers in the feed decompose thermally by a two-step mechanism under the separation of almost quantitative yield of cyclohexylisocyanate ($C_6H_{11}NCO$). Residues after the removal of $C_6H_{11}NCO$ are thermally stable nanoporous crosslinked copolymers of acryl-cyclohexylamide (A-CHA) with EDMA which decompose by a one-step mechanism between 300 and 450°C. In an attempt to compare the thermal properties of nanoporous poly(A-CHA-co-EDMA) with a nonporous model compound prepared by copolymerization of A-CHA with EDMA it was found that both compounds have almost the same thermal stability as proved by thermogravimetric analysis.

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747

INTRODUCTION

Nanotechnology is becoming a significant part of the 21st century's development. Novel properties of nanoparticles occur between the size of single molecules and about 100 nm. Nanoparticles can be prepared by size reduction or by the size increase. However, both of these methods produce particles of statistical distribution of size and size depending properties, what often leads to the aggregation of particles.[1] One especially suitable technique for the preparation of stable particles of various molecules is the molecular imprinting of the desired molecules into selected solid materials. During the last few decades, molecular imprinting of desired molecules into synthetic polymers has attracted a great deal of attention. This technique is of interest not only from a theoretical point of view, but it often has practical application, especially as a stationary phase in the thin layer chromatography,[2] as tailor made separation materials, enzyme mimics or catalytically active polymers in enzyme technology and organic synthesis, and as sensors in biosensors like configurations, where the polymers are used as substitutes for the biological materials normally employed.[3]

The molecular imprinting procedure described in the present paper is based on the selective thermal decomposition of crosslinked derivatives of acryl-dicyclohexylurea (A-DCU). The mechanism of this reaction is described in recently published papers,[4,5] in which we have shown that the homopolymer of *N*-acryl-*N*, *N*′-dicyclohexylurea (A-DCU) or copolymer with α-methylstyrene or styrene, thermally decomposes by a two-step mechanism. In the first step at a temperature of about 200°C, cyclohexylisocyanate separates ($C_6H_{11}NCO$) under the formation of thermally stable poly(acryl-cyclohexylamides) (A-CHA), or the corresponding copolymer with α-methylstyrene and styrene.

Following the reaction described in Ref.[4] we recently published a short note describing the preparation of crosslinked copolymers of A-DCU with ethylene glycole dimethacrylate (EDMA) and found that the highly crosslinked unswellable copolymers also decomposed thermally by a two-step mechanism under the separation of $C_6H_{11}NCO$.[6] After the removal of volatile cyclohexylisocyanate, the solid crosslinked poly(A-CHA-co-EDMA) which contains nanopores is formed by selective thermal degradation of dicyclohexylurea.

In order to a get better insight into the mechanism of the synthesis of crosslinked copolymers and to prepare poly(A-CHA), which contains various amounts of imprints in the solid crosslinked matrix, we have prepared copolymers of A-DCU with EDMA at different monomer to monomer ratios in the feed.

At the end of this paper, we compared the properties of nanoporous crosslinked copolymer of A-CHA with EDMA with those of nonporous poly(A-CHA-co-EDMA) of the same molar composition. Monomer A-CHA was prepared by condensation of acrylic acid anhydride with $C_6H_{11}NH_2$ and was identical with a product prepared by Plaut and Ritter in 1951 by condensation of acrylonitrile with cyclohexanol.[7]

EXPERIMENTAL

Synthesis of *N*-Acryl-cyclohexylamide

A solution of 4.95 g (5.7 mL; 0.05 mol) of $C_6H_{11}NH_2$ in 25 mL of ether was added slowly, not exceeding 10°C, to a solution of 6.3 g (0.05 mol) of acrylic acide anhydride and 0.2 g of hydroquinone in 50 mL of ether. After standing overnight at room temperature, the solution was left overnight in a refrigerator. The crystalline product was removed by filtration, yielding 5.54 g (72%) of a sharp melting product. The crude product was dissolved in 7 mL of chloroform and crystallized by the slow addition of 50 mL of petrolether (b.p. 40–60°C). After standing overnight in the refrigerator, the white shining crystals were filtered off yielding 4.0 g (52.3%) of an analytically pure product melting at 114°C (lit. m.p. 112–113°C).[7]

Analysis: Calcd. for $C_9H_{15}NO$ (153) (%): C, 70.59; H, 9.80; N, 9.15. Found: C, 70.29; H, 9.93; N, 9.03.

Polymerization Procedure

Copolymerization of A-DCU with EDMA at Molar Ratio of 0.3 to 0.7

To a mixture of 0.1668 g (0.0006 mol) of A-DCU and 0.2772 g (0.0014 mol) of EDMA was added 2 mL of butanone, which contains 1% (0.004 g) of dibenzoyl peroxide (Bz_2O_2). The reaction mixture was homogenized under the stream of nitrogen and heated for 20 hours at 70°C. After cooling, the copolymer was washed with butanone, yielding 0.4392 g (98.92%) of insoluble and unswellable crosslinked copolymer.

Under the same experimental conditions, the crosslinked copolymers of A-DCU with EDMA at a different monomer to monomer ratio in the feed were prepared and their properties are presented in Table 1.

A sample of copolymer prepared at a molar ratio of comonomers of 0.5 to 0.5 was heated on the glass plate of Fisher-Johnes Melting Point Apparatus, and it was observed that sample partially melts at about 200°C and strongly irritates eyes.

Copolymerization of A-CHA with EDMA at Molar Ratio of 0.5 to 0.5;
Nonporous Poly(A-CHA-co-EDMA) Model Compound

To a mixture of 0.306 g (0.002 mol) of A-CHA and 0.396 g (0.002 mol) of EDMA was added 2 mL of butanone which contains 1% (0.0004 g) of Bz_2O_2, and after heating for 20 hours at 70°C, the copolymer was washed with butanone, yielding 0.702 g (100%) of insoluble copolymer.

Analysis: Calcd. for $C_{19}H_{29}NO_5$ (351) (%): C, 64.96; H, 8.26; N, 3.99. Found: C, 63.17; H, 8.28; N, 3.79.

A sample of model copolymer did not change up to the temperature of 270°C when heated on the melting point apparatus.

Table 1. Elemental analysis of crosslinked copolymers of A-DCU with EDMA obtained at different monomer-to-monomer ratios in the field, theoretical and measured values of $C_6H_{11}NCO$ in copolymers.

A-DCU/EDMA (molar ratio)	Yield (%)	Calculated (%)	Found (%)	$C_6H_{11}NCO$ (%)	
				Theoretical values	Based on thermograms at 230°C
0.3/0.7	98.92	C, 63.78	C, 62.85	15	17.0
		H, 7.93	H, 7.91		
		N, 3.78	N, 3.58		
0.5/0.5	98.72	C, 65.58	C, 65.58	21	26.3
		H, 8.21	H, 8.49		
		N, 5.89	N, 5.74		
0.7/0.3	98.52	C, 67.08	C, 66.67	30.5	34.4
		H, 8.82	H, 8.95		
		N, 7.72	N, 7.55		
0.8/0.2	98.17	C, 67.7	C, 66.52	35.4	38.1
		H, 9.01	H, 9.07		
		N, 8.55	N, 8.25		

Preparation of Nanoporous Crosslinked Poly(A-CHA-co-EDMA) by Thermal Degradation of Poly(A-DCU-co-EDMA) Under the Separation of Cyclohexylisocyanate ($C_6H_{11}NCO$)

Under the previously described procedure at molar ratio of comonomers in the feed of 0.5 to 0.5, 1 g of crosslinked nanoporous copolymer prepared by the copolymerization was heated for 20 min at 200–240°C values in vacuum of 0.26 kPa (2 mmHg) yielding 0.7065 g of nanoporous poly(A-CHA-co-EDMA).

Analysis: Calcd. for $C_{19}H_{29}NO_5$ (351) (%): C, 64.94; H, 8.26; N, 3.99. Found: C, 63.43; H, 8.31; N, 4.01.

The theoretical amount of $C_6H_{11}NCO$ in poly(A-DCU-co-EDMA) is 0.263 g (26.3%), while the experimentally removed volatile fraction was 0.2935 g (29.35%).

Analysis: Calcd. for $C_6H_{11}NCO$ (125) (%): C, 67.21; H, 8.80; N, 11.20. Found: C, 67.28; H, 8.74; N, 11.04.

When heated on the Fisher-Johnes Melting Point Apparatus the nanoporous sample slightly changes at a temperature of 150–190°C and partially melts at 270°C.

Physicochemical Measurements

NMR spectra were obtained on a Varian EM 390 spectrometer. The copolymer composition was determined by elemental analysis. Differential scanning calorimetry was carried out on a Perkin Elmer model DSC-2 with a scanning rate of 40°C/min in nitrogen with the sample size of 15 mg. A glass transition temperature was taken as the half-height of the corresponding heat capacity jump. 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.

RESULTS AND DISCUSSION

Thermograms of copolymers described in the experimental part and presented in Fig. 1 indicate that regardless of the ratio of comonomers, copolymers decompose by a two-step mechanism. The first step starts in all cases at about 200°C. As is evident from thermograms in Fig. 1, the amount of $C_6H_{11}NCO$ separated at 230°C is in good agreement with a theoretical amount of $C_6H_{11}NCO$ (Table 1).

In order to compare the thermal stability of copolymers of A-DCU-co-EDMA with different monomer-to-monomer ratios in the feed, all four copolymers were heated for 5 min at 250°C in a thermogravimetric analyzer, and after removal of $C_6H_{11}NCO$, the thermograms of residual copolymer were determined and illustrated in Fig. 2. It is evident that there is no significant difference of thermograms of nanoporous copolymers which contain a different monomer-to-monomer ratio in the feed.

The comparison of the theoretical amount and experimentally determined $C_6H_{11}NCO$ shown in Fig. 3 indicates relatively good agreement. No attempt was made so far to optimize the results.

A comparison of thermograms of nanoporous residue obtained after heating 5 mg of poly(A-DCU-co-EDMA) for 5 min at 250°C, and the nonporous model compound
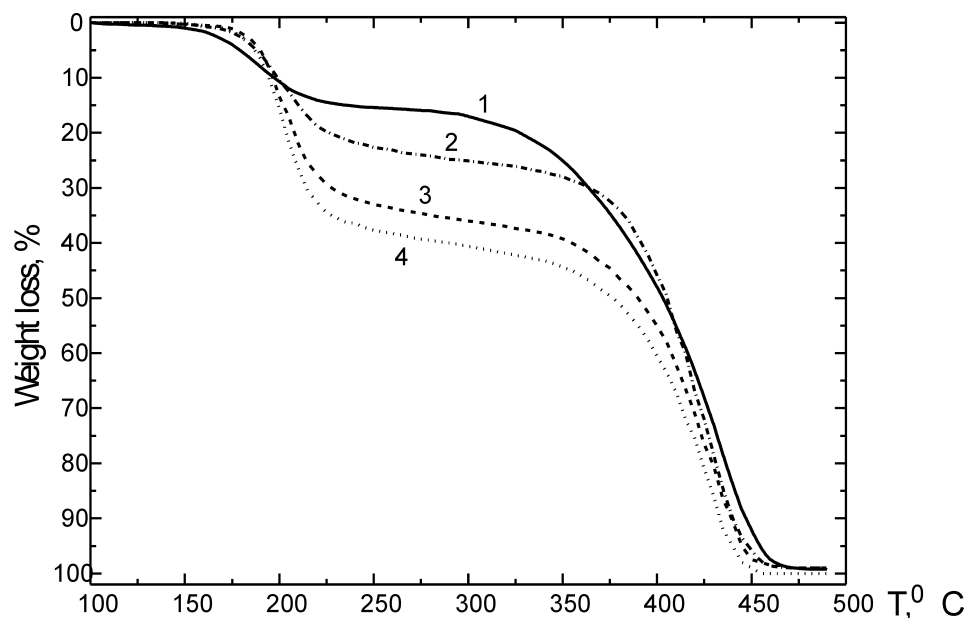

Figure 1. Thermograms of the crosslinked copolymers of A-DCU with EDMA at molar ratios in the feed: 0.3 to 0.7 (1); 0.5 to 0.5 (2); 0.7 to 0.3 (3); 0.8 to 0.2 (4).
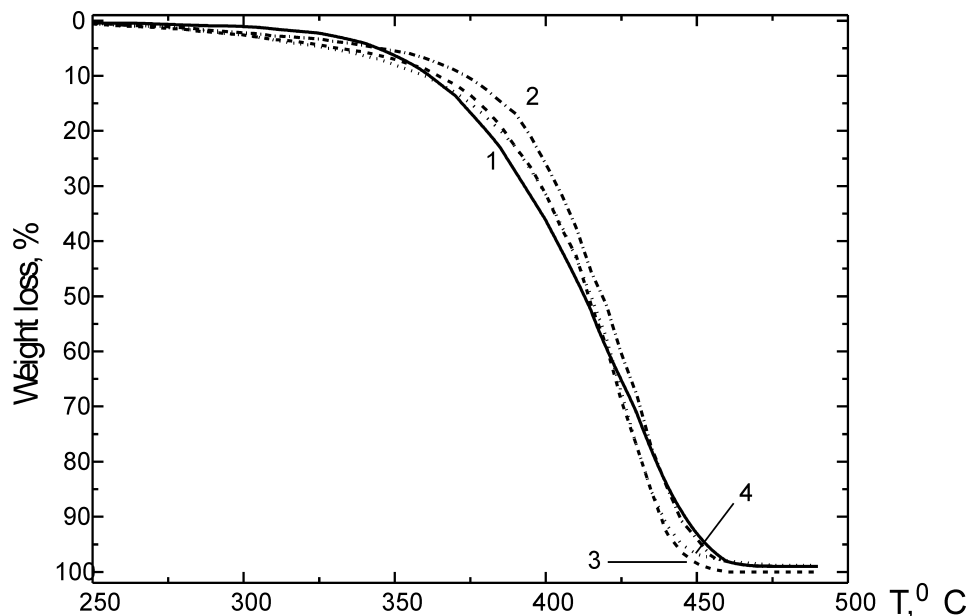
Figure 2. Thermograms of the nanoporous residues after removal of $C_6H_{11}NCO$ from the copolymers of A-DCU with EDMA at molar ratios of: 0.3 to 0.7 (1); 0.5 to 0.5 (2); 0.7 to 0.3 (3); and 0.8 to 0.2 (4).

poly(A-CHA-co-EDMA) is presented in Fig. 4. It is evident that both copolymers have nearly the same thermal stability, thus indicating that nanoimprints have no significant influence on the thermostability of crosslinked copolymers. However, DSC measurements show a big difference in the glass transitions of these two copolymers. Tg of nanoporous residue, poly(A-DCU-co-EDMA), is 228°C, while Tg of nonporous model copolymer is 302°C. This result was expected since the model compound is more compact than the nanoporous crosslinked copolymer. This is also in agreement with the qualitative data observed by measuring the melting properties on the melting point apparatus.

CONCLUSION

Acryl-dicyclohexylurea and EDMA were copolymerized to a high conversion under the formation of crosslinked copolymers at molar ratios of monomer-to-monomer in the feed: 0.3/0.7; 0.5/0.5; 0.7/0.3 and 0.8/0.2.

In a thermogravimetric analysis, all prepared copolymers decompose by a two-step mechanism under the separation of almost a quantitative yield of $C_6H_{11}NCO$ at a temperature between 200 and 230°C.

The residues alternated after the removal of $C_6H_{11}NCO$, decompose by a one-step mechanism in the temperature range of 300 and 450°C.
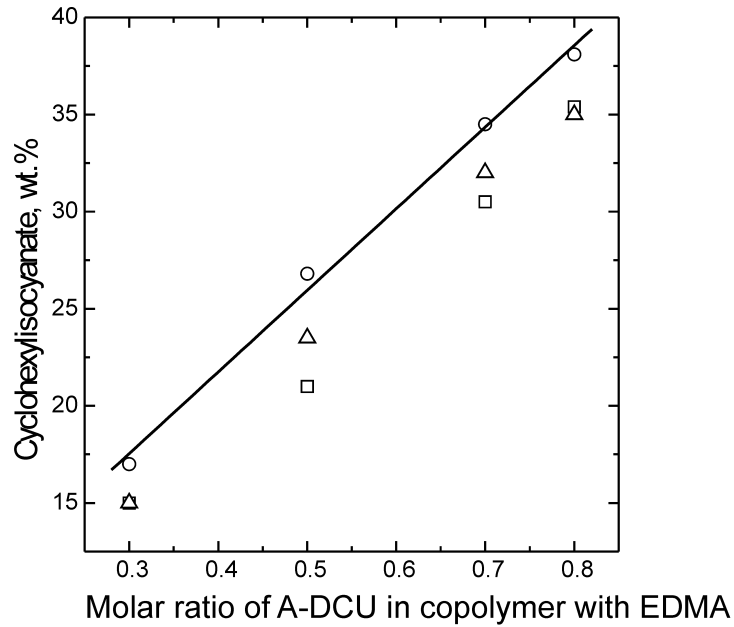
Figure 3. Comparison of theoretical and experimental values of $C_6H_{11}NCO$ obtained by thermal degradation of poly(A-DCU-co-EDMA): (○) theoretical values; (□) from thermograms at 230°C (Fig. 1); (△) from thermograms heated for 5 min at 250°C.
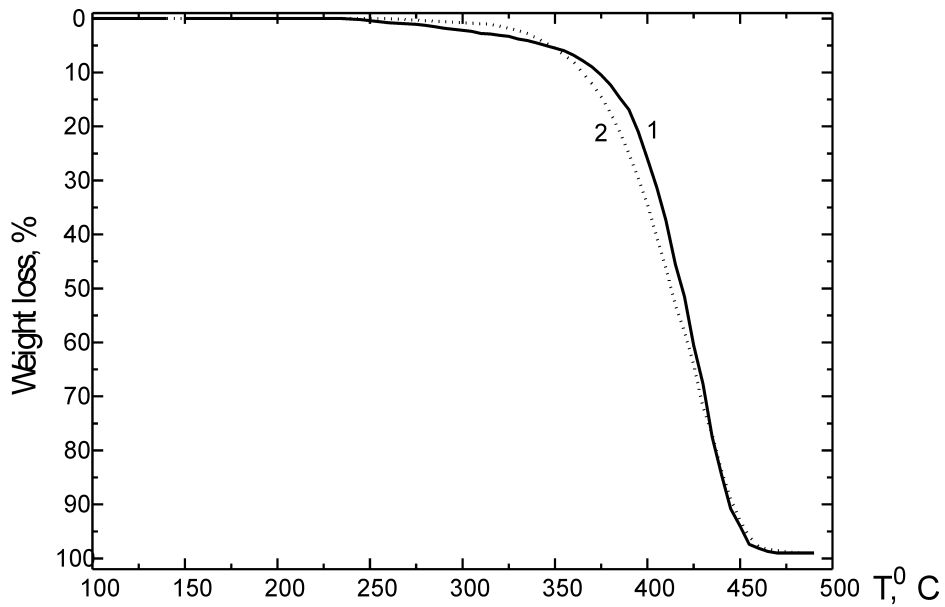

Figure 4. Thermograms of nanoporous poly(A-CHA-co-EDMA) (1) and nonporous poly(A-CHA-co-EDMA) (2).

There was practically no difference in the thermal decomposition of the residue which contains nanopores and synthetic model copolymer of A-CHA and EDMA. As expected, the Tg of nanoporous residue was lower (228°C) than the Tg of model compound (302°C).

ACKNOWLEDGMENT

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