Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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Online publication date: 20 February 2003

To cite this Article Kuzmić, Ana Erceg , Vuković, Radivoje , Bogdanić, Grozdana and Fleš, Dragutin(2003) 'Separation of Cyclohexylisocyanate from the Crosslinked Copolymers of N-Acryl-dicyclohexylurea with Ethylene Glycol Dimethacrylate or Divinyl Benzene', Journal of Macromolecular Science, Part A, 40: 1, 81 — 85
To link to this Article: DOI: 10.1081/MA-120016675
URL: http://dx.doi.org/10.1081/MA-120016675

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JOURNAL OF MACROMOLECULAR SCIENCE®
Part A—Pure and Applied Chemistry
Vol. 40, No. 1, pp. 81–85, 2003

NOTE

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ABSTRACT

Copolymerization of N-acryl-N,N′-dicyclohexylurea with ethylene glycol dimethacrylate or divinyl benzene in the presence of dibenzoyl peroxide as initiator gave corresponding crosslinked copolymers. Both copolymers thermally decompose by two-step mechanism. The first step separates cyclohexylisocyanate, thus forming the thermostable residue, which contains molecular imprints of cyclohexylisocyanates.

Key Words: N-Acryl-N,N′-dicyclohexylurea; Poly[(N-acryl-N,N′-dicyclohexylurea)$_2$-co-ethylene glycol dimethacrylate]; Poly[(N-acryl-N,N′-dicyclohexylurea)$_2$-co-divinyl benzene]; Mechanism of copolymerization; Thermal properties; Molecularly imprinted crosslinked copolymers.

INTRODUCTION

In continuation of our previous work on the polymerization on N-acryl-N,N′-dicyclohexylurea (Acryl-DCU) and N-methacryl-N,N′-dicyclohexylurea

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DOI: 10.1081/MA-120016675 1060-1325 (Print); 1520-5738 (Online)

(Methacryl-DCU) and copolymerization with styrene or α-methylstyrene (α-MeSt),[1,2] we are reporting in this note the preparation of crosslinked copolymers of Acryl-DCU with ethylene glycol dimethacrylate (I) or divinyl benzene (DVBz) (II). Our interest for the preparation of these compounds stems from the fact that poly(Acryl-DCU) and copolymers with α-MeSt are thermally stable materials which decompose between 180 and 450°C by the two step mechanism under the separation of cyclohexylisocyanate ($C_6H_{11}NCO$) at temperature of 180–250°C. Similarly it was found that by heating crosslinked copolymers I and II up to the temperature of 300°C when cyclohexylisocyanate is separated, the following crosslinked thermostable residues remain: poly[(cyclohexylacrylamide)$_2$-co-ethylene glycol dimethacrylate] and poly[(cyclohexylacrylamide)$_2$-co-divinyl benzene]. The thermostable residue contain molecularly imprinted structure.

EXPERIMENTAL

Preparation of Crosslinked Poly [(Acryl-DCU)$_2$-co-Ethylene Glycol Dimethacrylate] (I)

Acryl-DCU (0.556 g, 0.002 mol) was mixed with 0.198 g (0.001 mol) of ethylene glycol dimethacrylate (Aldrich), the mixture was dissolved in 2 mL of butanone and heated for 20 hrs at 70°C in the presence of 1% of dibenzoyl peroxide as initiator. The insoluble white copolymer was filtered off, yielding 0.69 g (91%) of hard insoluble material which swells in benzene, DMF and $CHCl_3$, but is unswellable in dioxane and dimethylsulfide.

Analysis: Calculated for crosslinked copolymer I: $C_{42}H_{66}N_4O_8$ (755.42); (%): C, 66.86; H, 8.75; N, 7.16. Found (%): C, 65.94; H, 8.53; N, 7.11.

Preparation of Crosslinked Poly[(Acryl-DCU)$_2$-co-DVBz] (II)

Acryl-DCU (0.556 g, 0.002 mol) was mixed with 0.130 g (0.001 mol) of DVBz (Aldrich) in 2 mL of butanone and heated for 22 hrs at 70°C in the presence of 1% of dibenzoyl peroxide as initiator. Solvent was evaporated and the residue dried and analyzed. Yield 0.614 g (89.8%). The residue behaves in different solvents in the same manner as pointed out for copolymer I.

Analysis: Calculated for crosslinked copolymer II: $C_{42}H_{62}N_4O_4$ (686.42); (%): C, 73.49; H, 9.03; N, 8.16. Found (%): C, 71.99; H, 9.25; N, 7.96.

RESULTS AND DISCUSSION

Thermogravimetric analysis of crosslinked copolymers poly[(Acryl-DCU)$_2$-co-ethylene glycol dimethacrylate] (I) and poly[(Acryl-DCU)$_2$-co-DVBz] (II) are presented

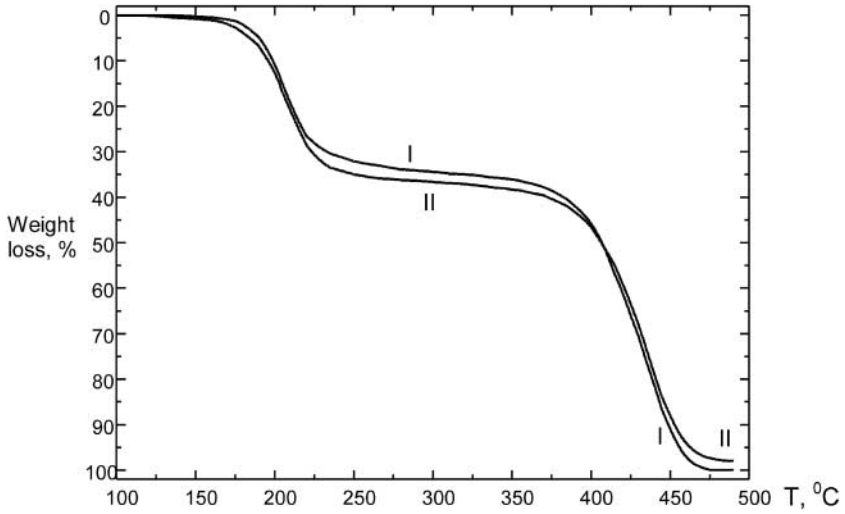

Figure 1. Thermogravimetric analysis of poly[(acryl-DCU)$_2$-co-ethylene glycol dimethacrylate] (I) and poly[(acryl-DCU)$_2$-co-DVBz] (II) at molar comonomers ratio of 1:1.

in Fig. 1. It is evident that both copolymers decompose by two-step mechanism with sharp ceiling temperature. The loss of weight between 180–220°C is 30% for copolymer I and 32% for copolymer II, what closely corresponds to the content of cyclohexylisocyanate: 31.6% in I and 32.7% in II. The residues after the removal of $C_6H_{11}NCO$ have the following elemental analysis:

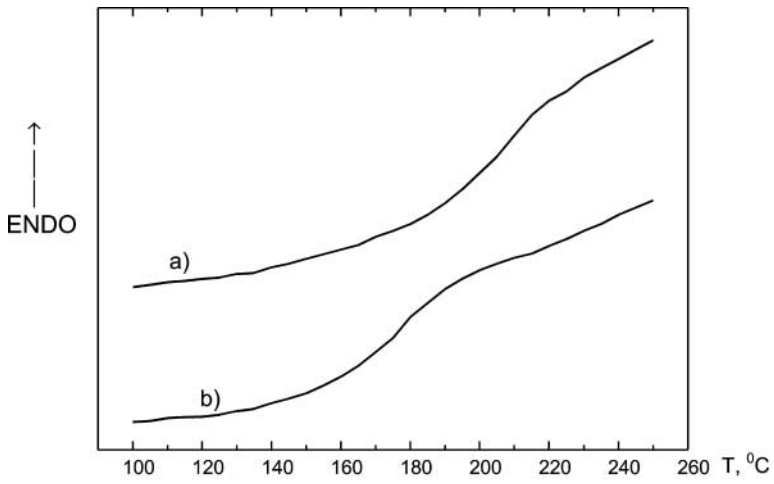

Figure 2. DSC curves of the crosslinked copolymer residues after the removal of cyclohexylisocynate from copolymers I and II: a) poly[(cyclohexylacrylamide)$_2$-co-ethylene glycol dimethacrylate] and b) poly[(cyclohexylacrylamide)$_2$-co-DVBz].

Residue of copolymer I, (a): Calculated for poly[(cyclohexylacrylamide)$_2$-co-ethylene glycol dimethacrylate]: $C_{28}H_{44}N_2O_2$ (504.28); (%): C, 66.68; H, 8.73; N, 5.55. Found (%): C, 64.62; H, 8.66; N, 5.62.

Residue of copolymer II, (b): Calculated for poly[(cyclohexylacrylamide)$_2$-co-DVBz]: $C_{28}H_{40}N_2O_2$ (436.28); (%): C, 77.08; H, 9.27; N, 6.42. Found (%): C, 74.05; H, 6.19; N, 6.74.

Concerning elemental analyses it must be emphasized that samples of thermostable residues of the thermogravimetric analyses were not purified, and for this reason, the values of carbon atoms significantly differ from theoretical ones. It is, however, of importance to note that contents of nitrogen in residues of both samples I and II after the removal of cyclohexylisocyanate, closely correlate to theoretical values which are much lower than the values of nitrogen in crosslinked copolymers containing Acryl-DCU.

The residues of both copolymers are stable up to 300°C and decompose by one step mechanism up to temperature of 450°C. T_g's of residues determined by DSC are 204°C for copolymer I, (a) and 177°C for copolymer II, (b). DSC curves are presented in the Fig. 2.

CONCLUSION

Short introductory part and examples of syntheses of crosslinked copolymers that under controlled heating almost quantitatively lose cyclohexylisocyanate enable the formation of thermally stable molecularly imprinted residues. In view of the possibility to modify the copolymer composition and geometry of N,N′-disubstituted urea we consider that these copolymers may be of interest as hosts specific for desired molecules for various applications, especially in various types of thin layer chromatography separation.[3]

ACKNOWLEDGMENTS

The Ministry of Science and Technology of Croatia supported this work.

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Received August 13, 2002