## Structural Differences Between Copolymers of Acryl- and Methacryl-dicyclohexylurea with Ethylene Glycol Dimethacrylate and their Thermal Degradation Products

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*The present paper describes structural characteristics of crosslinked copolymers of acryl-dicyclohexylurea (A-DCU) and methacryl-dicyclohexylurea (MA-DCU) with ethylene glycole dimethacrylate (EDMA). Both copolymers decompose when heated at temperatures between 180–250°C under the separation cyclohexylisocyanate ($C_6H_{11}NCO$) yielding nanoporous copolymers of poly(A-CHA-co-EDMA) and poly(MA-CHA-co-EDMA). The comparison was also made between structural characteristics of crosslinked nanoporous copolymers of poly(A-CHA-co-EDMA) and poly(MA-CHA-co-EDMA) and nonporous crosslinked model compounds poly(A-CHA-co-EDMA) and poly(MA-CHA-co-EDMA).*

**Keywords** poly(acryl-dicyclohexylurea–co–ethylene glycol dimethacrylate), poly(methacryl-dicyclohexylurea–co–ethylene glycol dimethacrylate), nanoporous crosslinked copolymers, nonporous crosslinked copolymers, structure, thermal degradation

## Introduction

In recently published papers (1–4), we have described the synthesis and copolymerization of poly(N-acryl-N,N′-dicyclohexylurea) and poly(N-methacryl-N,N′-dicyclohexyl urea) with ethylene glycol dimethacrylate at different molar ratio of comonomers in the feed. All prepared crosslinked copolymers are thermally stable materials, which decompose between 180°C and 450°C by a two-step mechanism under the separation of cyclohexylisocyanate ($C_6H_{11}NCO$) at temperatures between 180–250°C. After the removal of cyclohexylisocyanate, the crosslinked nanoporous poly(acryl-N-cyclohexyl amide–co–ethylene glycol dimethacrylate) [poly(A-CHA-co-EDMA)] and poly(methacryl-N-cyclohexyl amide–co–ethylene glycol dimethacrylate) [poly(MA-CHA-co-EDMA)] are obtained.

In the present paper, we compared structural characteristics of poly(A-DCU-co-EDMA) and poly(MA-DCU-co-EDMA) with nanoporous crosslinked copolymers poly(A-CHA-co-EDMA) and poly(MA-CHA-co-EDMA). At the same time, we have also compared structural characteristics of mentioned copolymers with nonporous copolymers poly(A-CHA-co-EDMA) and poly(MA-CHA-co-EDMA).

## Experimental

### Synthesis of Copolymers

N-Acryl-N,N′-dicyclohexylurea (A-DCU) and N-methacryl-N,N′-dicyclohexylurea (MA-DCU) were copolymerized with ethylene glycol dimethacrylate (EDMA) at different monomer to monomer ratios in the feed in butanone in the presence of dibenzoyl peroxide up to high conversion as described in References (1–3).

Nanoporous copolymers of poly(A-DCU-co-EDMA) and poly(MA-DCU-co-EDMA) were prepared by thermal degradation of corresponding copolymers under the separation of cyclohexylisocyanate ($C_6H_{11}NCO$) as described in References (2, 3).

In order to deduce structural differences between original acrylic copolymer A-DCU-co-EDMA and its thermal degradation product (A-CHA-co-EDMA), we also synthesized the nonporous copolymer compounds with the same repeating units A-CHA-co-EDMA (2). A similar structural comparison was performed by methacrylic copolymers with MA-DCU-co-EDMA and MA-CHA-co-EDMA (4). In this way, structural characterization follows the comparison of two systems (acrylic and methacrylic) with three compounds specified in Figures 1 and 2.
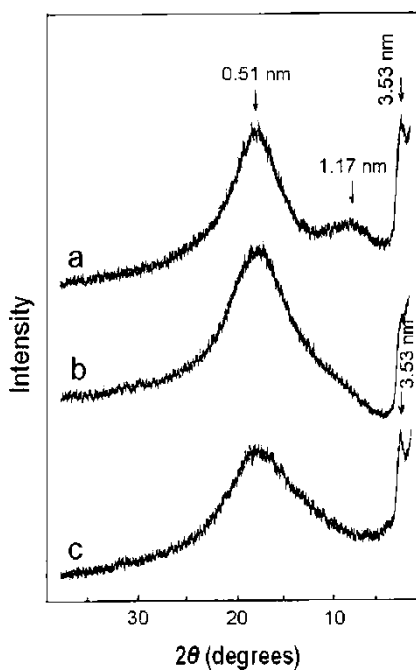


**Figure 1.** WAXD diffractograms of acrylic copolymers: original poly(A-DCU-co-EDMA) (a), imprint poly(A-CHA-co-EDMA) (b), and model poly(A-CHA-co-EDMA) copolymer (c).
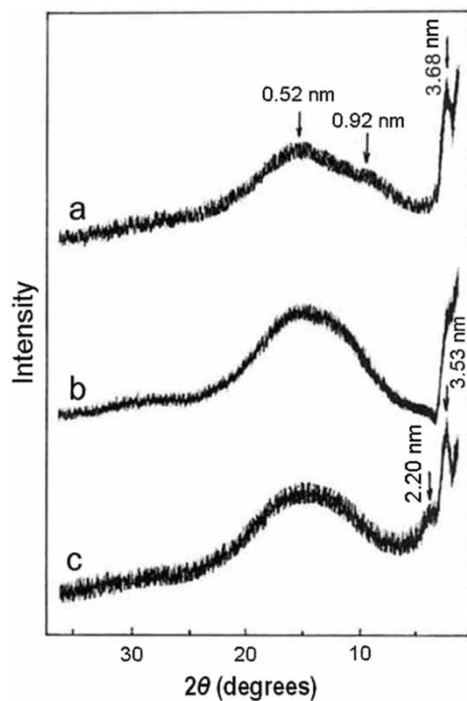
**Figure 2.** WAXD diffractograms of methacrylic copolymers: original poly(MA-DCU-co-EDMA) (a), imprint poly(MA-CHA-co-EDMA) (b), and model poly(MA-CHA-co-EDMA) copolymer (c).

## Methods of Characterization

Structural characterization of the samples was performed by X-ray diffraction by a Philips diffractometer with monochromatized CuK$_\alpha$ radiation. Diffractograms at a lower diffraction angle were taken by using narrow entrance slit. Polarization micrographs were given by optical microscopy (Leica, Model DMLS) equipped with a video camera.

## Results and Discussion

### X-ray Diffraction (XRD)

X-ray diffractogram of poly(A-DCU-co-EDMA) sample prepared at 0.5 to 0.5 molar ratio of comonomers in the feed exhibits two expressive diffuse maxima with tops at 7.55 and 17.4°$2\Theta$, which correspond to the amorphous phase as shown in Figure 1(a). Interplanar spacings are calculated by the Bragg equation $d = 1.17$ and $0.51$ nm, respectively. The value of interplanar spacing of most intensive amorphous halo $d = 0.52$ nm is somewhat higher than characteristic for disordered liquid-like conformation of liquid paraffins ($d \approx 0.45$ nm) (5) and could be assigned to the structural characteristics of the main chain. A weaker first amorphous halo at about 7.55°$2\Theta$ ($d = 1.17$ nm) usually originated from diffraction on characteristic interchain distance (6). This diffractogram also reveals one sharp reflection in the small angle region with interplanar spacing $d = 3.53$ nm. This value indicates some kind of long periodicity ordering. The degree

of disorder for this peak ($\Delta/\bar{a} = \Delta/d$) can be obtained from the expression proposed by Vainshtain (7):

$$\Delta/d = \frac{1}{\pi}\sqrt{\frac{\beta_s d}{\lambda}} \tag{1}$$

where $\Delta$ is the mean-square deviation of distances between the neighboring molecules, $d$ is spacing, $\beta_s$ is half maximum width in radians of the peak observed at mean diffraction angle $2\theta$ and $\lambda = 0.1547\,nm$ is the wavelength of X-rays.

The degree of disorder $\Delta/d = 0.135$ calculated from a half maximum width of this reflection ($\beta_s = 0.45°\Theta$) is lower than the limit value $\Delta/d = 0.2$ bellow in which a strong first maximum could arise. This fact confirms long distance ordering and close packing of domains, regardless of its shape (lamellae, cylinders, spheres) with disordered conformation of side chains inside these domains.

A diffractogram of nanoporous poly(A-CHA-co-EDMA) copolymer given by thermal degradation (Figure 1b) differs obviously from this one of original poly(A-DCU-co-EDMA) sample (Figure 1a). In comparison to diffractogram 1a, a sharp first reflection in diffraction curve 1b is omitted and a first amorphous halo at $7.55°2\Theta$ attenuates, shifts to higher angles, and merges with a more intensive halo at $17.4°2\Theta$. It seems that the breaking side chains in poly(A-DCU-co-EDMA) macromolecules and presumable outgoing of cyclohexylisocyanate units by thermal degradation disturbs the close packing of macromolecules in domains that leads to losing the characteristic long distance ordering in the "imprint" sample.

The diffraction curve of poly(A-CHA-co-EDMA) ("model" sample) (Figure 1c) is more similar to the one of the original sample (Figure 1a) than to the diffractogram of the imprint poly(A-CHA-co-EDMA) sample (Figure 1c), although the macromolecule of the model samples are supposed to be the same. Diffractogram 1c consists of sharp reflection in the small angle region (3.53 nm) and one expressive diffuse maximum with the highest at $17.4°2\Theta$ ($d = 0.51\,nm$) analogously to the poly(A-DCU-co-EDMA) sample. In distinction to the diffractogram 1a, the first amorphous halo in the diffractogram 1c is either omitted or mainly overlapped with an intensive diffuse halo. The degree of disorder of the first peak $\Delta/d = 0.12$ is lower than the corresponding value $\Delta/d = 0.135$ for the original A-DCU-co-EDMA sample. A low degree of disorder proves that the first diffraction maximum, as a reflection, indicates close packing with long distance ordering ($d = 3.53\,nm$) in the model A-CHA-co-EDMA sample, as well.

Diffractograms of methacrylic copolymers (Figure 2) show similarity with those of acrylic copolymers in Figure 1. The diffraction curve of poly(MA-DCU-co-EDMA) sample also exhibits two expressive diffuse amorphous halos with peaks at 9.6 and $17.1°2\Theta$ (with interplanar spacings $d = 0.92$ and $0.52\,nm$, respectively) and one sharp reflection in the small angle region (3.68 nm) as shown in Figure 2a. The first amorphous halo at $9.6°2\Theta$ ($d = 0.92\,nm$) is shifted and partially overlapped with a more intensive second amorphous halo.

A diffractogram of the imprint poly(MA-CHA-co-EDMA) sample (Figure 2b), given by thermal degradation of the original methacrylic copolymer, exhibits mainly one expressive diffraction halo similar to the diffractogram of the corresponding imprint sample of acrylic copolymers presented with curve 1b. The first sharp reflection in diffraction curve 2b is omitted similarly to the diffractogram of the acrylic imprint copolymer poly(A-CHA-co-EDMA). The diffractogram of poly(MA-CHA-co-EDMA) ("model" sample) (Figure 2c) consists of a sharp reflection (3.53 nm) and from one expressive

amorphous halo with the peak at $17.1°2\Theta$ ($d = 0.52$ nm) similar to the corresponding acrylic poly(A-DCU-co-EDMA) sample (Figure 1c). Additionally, diffraction curve 2c contains an uncertain weak peak at low angle ($d = 2.20$ nm) in comparison to diffraction curve 1c. The degree of disorder for both copolymers (poly(MA-DCU-co-EDMA)–curve 2a) and (poly(MA-CHA-co-EDMA)–curve), (2c) calculated from half maximum widths of first reflection $\Delta/d = 0.12$ is also lower than the limit value $\Delta/d = 0.2$ bellow, where a strong first maximum could arise. It means that long distance ordering arises in these samples, whereas this ordering is disturbed by thermal degradation, i.e., in the "imprint" poly(MA-CHA-co-EDMA) sample.

### Polarizing Microscopy

Powder of the copolymer samples were inspected between crossed polarizers in order to detect optical anisotropy of copolymer phases. Polarized micrographs of acrylic copolymers are presented in Figures 3a, b, c. Micrograph of the original poly(A-DCU-co-EDMA) sample in Figure 3a reveals bright grains, whereas the grains of the imprint poly(A-CHA-co-EDMA) sample becomes darker (Figure 3b). The powder of model poly(A-CHA-co-EDMA) sample shines (Figure 3c) similarly to the powder of the original sample. Polarized micrographs of methacrylic copolymers show similarity with those of acrylic copolymers in Figures 3a–c.

Brightness of specimens in polarized micrographs originates from anisotropy of optical properties due to the birefringent character of consisting domains (ordered crystalline or mesostructural regions), as well as under circumstances where non-crystalline samples are subjected to some form of stress field liquid crystals, flowing or sheared melts, polymers in solution and deformed glasses) (8, 9).

Obviously, the powder grains of original and model acrylic and methacrylic copolymers shines between crossed polarizers because long distance ordering of the domains confirmed by WAXD (with presumable lamellar or rod-like shape) causes the anisotropy of optical properties. Imprint poly(A-CHA-co-EDMA) and poly(MA-CHA-co-EDMA) samples exhibit a pattern with some degree of the extinction due to outgoing of cyclohexylisocyanate units by thermal degradation of the original sample. It causes the rising of the microvoids between condensed macromolecules and demarcation line between packed macromolecules and domains becomes more irregular. The disappearance of long distance ordering is likely due to disturbed close packing of macromolecules and domains as was confirmed by WAXD. In spite of losing long distance ordering, the grains of imprint acrylic and methacrylic samples retain some degree of optical anisotropy since they retain preferential orientation of condensed macromolecules or even domains. As a consequence, the grains of imprint acrylic and methacrylic samples are partially bright.
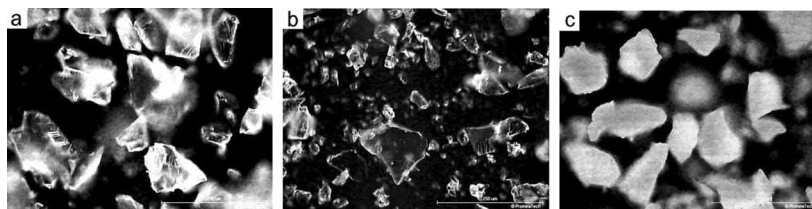


**Figure 3.** Polarizing micrographs of acrylic copolymers: original poly(A-DCU-co-EDMA) (a), imprint poly(A-CHA-co-EDMA) (b), and model poly(A-CHA-co-EDMA) copolymer (c).

## Conclusions

X-ray diffractograms and polarized light micrographs of imprint poly(A-CHA-co-EDMA) and poly(MA-CHA-co-EDMA) samples given by thermal degradation differ from the original acrylic poly(A-DCU-co-EDMA) and methacrylic poly(MA-DCU-co-EDMA) copolymers, as well as from model poly(A-CHA-co-EDMA) and poly(MA-CHA-co-EDMA) samples. WAXD diffractograms of imprint samples show a loss of long distance ordering in comparison to the original and model samples. It seems that the breaking of the side DCU chains in poly(A-DCU-co-EDMA) macromolecules and presumable outgoing of cyclohexylisocyanate units by thermal degradation causes the rising of imprint microvoids between condensed macromolecules inside domains. Rising of microvoids disturbs partially regular packing of lamellar or rod-like domains with irregular segmental packing of condensed macromolecules. The outgoing of cyclohexylisocynate takes place from condensed matter and that is the reason why imprint poly(A-CHA-co-EDMA) and poly(MA-CHA-co-EDMA) macromolecules retain preferential orientation still retaining the anisotropy of optical properties. As a result, the grains of imprint acrylic and methacrylic powders are partially bright. Additional information about domain shape (lamellar, cylindrical, spherical) and their supermolecular packing in the sample could be given by further research on small-angle X-ray scattering (SAXS) and atomic forced microscopy (AFM).

## Acknowledgments

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