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Ana Erceg Kuzmić^a; Grozdana Bogdanić^a; Radivoje Vuković^a

^a INA-Industrija nafte, d.d., Research and Development Sector, Lovinčičeva b.b., Zagreb, Croatia

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Copolymerization of N-*tert*-Butylacrylamide with Ethylene Glycol Dimethacrylate

ANA ERCEG KUZMIĆ, GROZDANA BOGDANIĆ, and RADIVOJE VUKOVIĆ

INA-Industrija nafte, d.d., Research and Development Sector, Lovinčićeva b.b., Zagreb, Croatia

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N-*tert*-butylacrylamide (NtBA) was copolymerized with ethylene glycol dimethacrylate (EDMA) in butanone solution over a wide composition and conversion range, using dibenzoyl peroxide (Bz₂O₂) as a free-radical initiator. The copolymer composition was determined from the nitrogen content. Using only low conversion ($\leq 20\%$) collected for the copolymerization reactions, monomer reactivity ratios were estimated using the Kelen-Tüdös graphical method and were found to be $r_1 = 0.26$ (NtBA) and $r_2 = 7.05$ (EDMA). In order to get a better insight into the mechanism of nanoporous copolymers of NtBA with EDMA preparation by thermal degradation of copolymers of N-acryl-N,N'-di-*tert*-butylurea (A-DitBuU) with EDMA, nanoporous copolymers (model compound), of the same chemical structure and composition, were prepared by performing copolymerization of NtBA with EDMA up to the high conversion of 97–100%. Thermal behavior of nanoporous and nonporous copolymers of NtBA with EDMA was studied.

Keywords: N-*tert*-butylacrylamide; ethylene glycol dimethacrylate; copolymerization; model compound

1 Introduction

Acrylamide-based polymers are of interest in many fields of polymer science, i.e., as plastic materials, water soluble polymers, polymeric additives, and comb-like polymers with molecular order in amorphous matrix, in gel preparation and as a crosslinking agent. In the previously published paper, we have described the synthesis and polymerization of N(*p*-phenoxyphenyl)acrylamide and copolymerization with styrene (1). These copolymers belong to the comb-like polymers which, due to the presence of mesogenic groups in the side chains, show the tendency to exhibit smectic ordering in the amorphous matrix. Another important field of the acrylamide based polymers study is gel preparation. The finding of a large volume change in response to an infinitesimal alternation in the environment has opened a wide variety of possible applications of gels as functional elements. For example, gels can be used as sensors, switches, or mechanochemical actuators and in drug delivery systems. In other words, the study on the swelling behavior of gels is very important in practical applications (2–5). The swelling and mechanical properties of hydrogels

can be controlled by modification of the polymer backbone structure and/or crosslinking density. N-*tert*-butylacrylamide is used as a component of interpenetrating network hydrogels (6), in stimuli-sensitive copolymer preparations (7), in synthesis of thermosensitive hydrogels (8), in preparation of crosslinking drug-delivery, pH-sensitive hydrogels (9–11). Another comonomer used in this study in the copolymerization reaction, ethylene glycol dimethacrylate (EDMA) belongs to the family of crosslinking agents based on ethylene glycol, for example: ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate and tetraethylene glycol diacrylate (12).

In our recently published papers, EDMA was used as a comonomer in the preparation of poly(acryl-N-cyclohexylamide-co-EDMA) (13), poly(methacryl-N-cyclohexylamide-co-EDMA) (14), and poly(methacryl-N-isopropylamide-co-EDMA) (15), which were used as model nonporous compounds in order to elucidate the mechanism of thermal degradation of the corresponding urea copolymers with EDMA. These are: poly(N-acryl-N,N'-dicyclohexylurea-co-EDMA), poly(N-methacryl-N,N'-dicyclohexylurea-co-EDMA), and poly(N-methacryl-N,N'-diisopropylurea-co-EDMA). Copolymerization of NtBA with EDMA was studied in this paper. By performing polymerization to a conversion below 20%, monomer reactivity ratios and initial polymerization rates were determined. In order to get a better insight into the mechanism of the nanoporous copolymers of NtBA with EDMA, prepared by thermal degradation of copolymers of

Address correspondence to: Radivoje Vuković, INA-Industrija nafte, d.d., Research and Development Sector, Lovinčićeva b.b., POB 555, 10002 Zagreb, Croatia. Fax: +385 1 2381 228; E-mail: radivoje.vukovic@ina.hr

A-DitBuU with EDMA (16), monomers NtBA and EDMA were polymerized up to high conversion (97–100%), thus crosslinked nonporous (model compounds) were prepared. Comparison was made between the thermal properties of nanoporous and nonporous copolymers. Since molecularly imprinted copolymers of NtBA with EDMA contain nanopores, it can be expected that corresponding nonporous model compounds are more compact, and thus exhibiting a different thermal behaviour (weight loss and transition temperature).

2 Experimental

2.1 Materials

N-tert-Butylacrylamide (NtBA), 97%, Sigma-Aldrich Chemie GmbH, Steinheim, Germany; Ethylene Glycol Dimethacrylate (EDMA), 98%, Aldrich, Steinheim, Germany; Butanone, p.a., Merck, Darmstadt, Germany; Chloroform, p.a., Kemika, Zagreb, Croatia; Methanol, p.a., Kemika, Zagreb, Croatia; Dibenzoyl Peroxide (Bz₂O₂), 97%, Fluka, Buchs, Switzerland.

2.2 Polymerization Procedure

Polymerization was performed in a butanone solution using dibenzoyl peroxide (Bz₂O₂) as the free-radical initiator, with reactions run in glass tubes (10 mL), thoroughly degassed, filled with nitrogen before sealing and placed into an oil bath thermostated at 70°C. When polymerization was carried out to a low conversion (≤20%) after a predetermined time, the mixture was cooled to the ambient temperature, diluted with chloroform and precipitated by dropwise addition to methanol. The recovered polymers were dried under vacuum at 60°C until a constant weight achieved. For polymerizations up to high conversions (97–100%) the ultimate mixture was washed with butanone in order to remove the unreacted monomers. In both cases, conversion was determined gravimetrically. The composition of copolymers was obtained from the nitrogen content.

2.3 Measurements

Elemental analysis was obtained by a LECO CHNS-932 automatic analyzer. Thermogravimetric analysis, TGA, was made with the Perkin-Elmer Pyris 6 TGA, in a nitrogen atmosphere with a heating rate of 10°C/min. Differential scanning calorimetry, DSC, was carried out on the Perkin-Elmer Diamond DSC, with a scanning rate of 40°C/min in nitrogen and sample size of about 10 mg. Glass transition temperature, T_g and T_{trans} (temperature above T_g), were taken as the inflection point of the heat capacity discontinuation in the first scan.

3 Results and Discussion

3.1 Low Conversion Polymerization

The procedure applied for the low-conversion copolymerization of NtBA with EDMA at the molar ratio of 0.5 to 0.5 in the feed was, as follows: to a mixture of 0.127 g (0.001 mol) of NtBA and 0.198 g (0.001 mol) of EDMA, 1 mL of butanone containing 0.2 wt% of Bz₂O₂ was added. The polymerization reaction was run for 45 min at 70°C in nitrogen. After cooling, the reaction mixture was diluted with chloroform, poured into methanol, and the copolymer was separated by filtration. It was then dried under vacuum at 60°C overnight, yielding 0.0807 g (16.54%) of copolymer. The results of the copolymerization of NtBA with EDMA at molar ratios: 0.3/0.7; 0.4/0.6; 0.5/0.5; 0.6/0.4; 0.7/0.3; 0.8/0.2 in the feed, are presented in Table 1.

It is evident that copolymer yield depends on the molar ratios of comonomers in the feed, as well as on the polymerization time. The data in Table 1 and Figure 1 show that the content of NtBA in copolymers is always lower than the content of EDMA.

From the data presented in Figure 1 for the copolymerization of NtBA with EDMA of different comonomer composition, the reactivity ratios, r₁ = 0.26 (NtBA) and r₂ = 7.05 (EDMA), are determined graphically (Figure 2) by using the Kelen-Tüdös Equation (1):

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

where η and ξ are functions of the molar fraction of monomers in copolymer and in the feed, respectively, and α is an arbitrary parameter (17).

The initial rate of copolymerization was calculated also from data in Table 1. It is evident that R_p decreases with increasing the content of NtBA monomer in the feed (Figure 3).

Table 1. Polymerization conditions and composition of NtBA with EDMA copolymers, obtained at different monomer-to-monomer ratios in the feed

Molar fraction of NtBA		Time (min)	Yield (g)	Conversion (wt%)	N (%)
In feed	In copolymer ^a				
0.30	0.060	35	0.0977	18.42	0.66
0.40	0.093	40	0.0921	18.09	1.02
0.50	0.117	45	0.0807	16.54	1.29
0.60	0.143	50	0.0648	13.89	1.57
0.70	0.307	120	0.0854	19.17	3.31
0.80	0.427	300	0.0994	20.00	4.70

1M/L; 0.2 % of Bz₂O₂ in butanone at 70°C; in nitrogen.

^aBased on the nitrogen content.

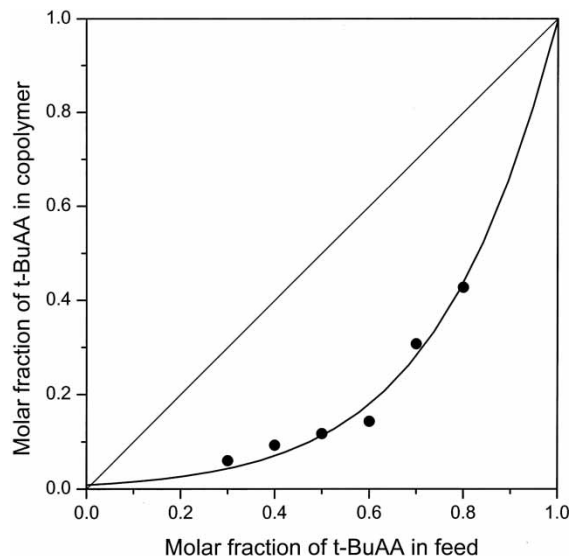


Fig. 1. Ratio of molar fraction of NtBA with EDMA in the feed and in the copolymer.

3.2 Synthesis of Nonporous Poly(NtBA-co-EDMA) Model Compounds

Nonporous copolymers of NtBA with EDMA of different monomer-to-monomer ratios were prepared under the previously described polymerization procedure by performing polymerization up to a high conversion. Free-radical solution polymerization in butanone was performed at 70°C, by using 2 wt% of Bz₂O₂ during 48 h. A typical experiment applied in the preparation of poly(NtBA-co-EDMA)

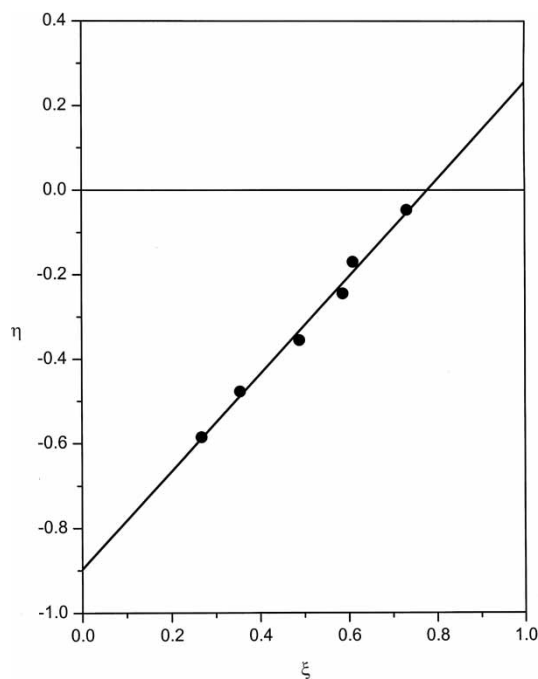


Fig. 2. Kelen-Tüdös diagram for calculation of reactivity ratios in the copolymerization of NtBA with EDMA.

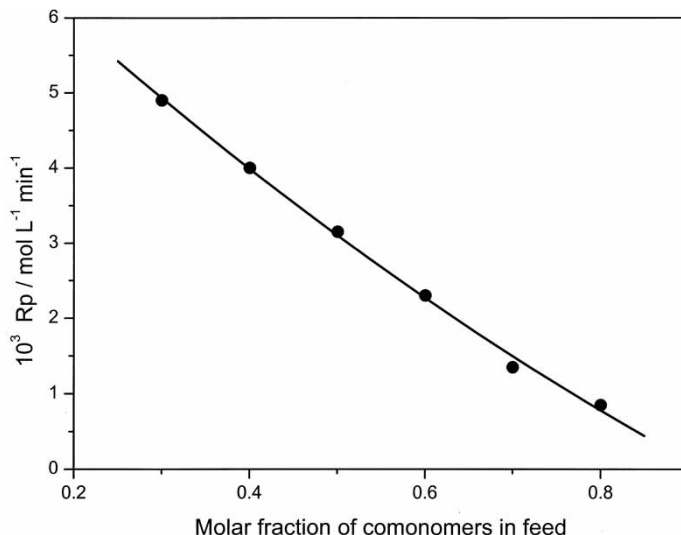


Fig. 3. Initial rate of copolymerization of NtBA with EDMA vs. molar fraction of monomers in feed.

copolymer at molar ratio of 0.5 to 0.5 in the feed consisted of the polymerization of 0.127 g (0.001 mol) of NtBA and 0.198 g (0.001 mol) of EDMA dissolved in butanone in the presence of 2 wt% of Bz₂O₂, at 70°C, during 48 h in nitrogen. After that, the resulting product was cooled to room temperature, washed with butanone and dried in the vacuum overnight at 60°C. The copolymer yield was 0.3149 g (97%). Under the same experimental conditions, the crosslinked copolymers of NtBA with EDMA at different monomer-to-monomer ratio in the feed were prepared, with properties presented in Table 2.

3.3 Thermal Behavior of the Copolymers of NtBA with EDMA

Thermal stability of poly(NtBA-co-EDMA) was investigated by TGA in a nitrogen atmosphere, with a heating rate of 10°C/min and a temperature range of 100 to 450°C.

Table 2. Polymerization conditions and composition of poly(NtBA-co-EDMA)

Molar fraction of NtBA		Yield (g)	Conversion (wt%)	Elemental analysis
In feed	In copolymer			
0.30	0.22	0.3464	98.0	C, 58.27 H, 7.98 N, 2.40
0.40	0.30	0.3371	99.3	C, 58.40 H, 8.21 N, 3.25
0.50	0.37	0.3149	97.0	C, 58.98 H, 8.58 N, 4.07
0.60	0.47	0.3085	99.2	C, 60.45 H, 8.67 N, 5.16
0.70	0.57	0.2924	98.5	C, 60.68 H, 9.03 N, 6.25
0.80	0.65	0.2711	97.0	C, 60.98 H, 9.27 N, 7.15

Polymerization conditions: 70°C; 2 wt% of Bz₂O₂; 48 h; N₂; 2M/L.

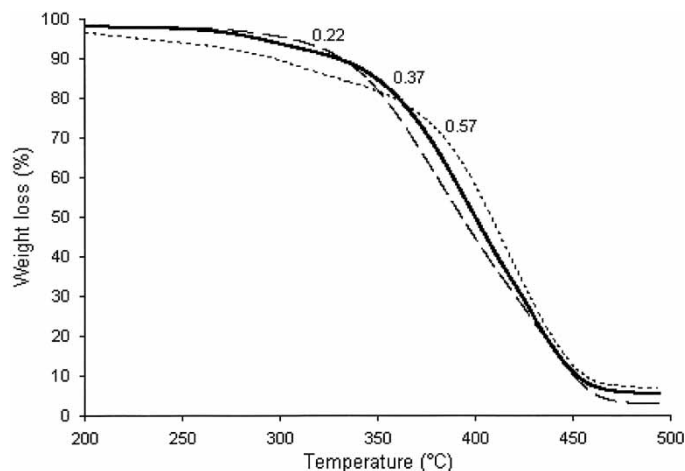


Fig. 4. Thermograms of the nonporous model copolymers of NtBA with EDMA, with NtBA molar ratio: 0.22; 0.37; and 0.57.

Thermograms of the copolymers of different monomer-to-monomer ratios are presented in Figure 4. The results show a high thermal stability for these copolymers. It is evident that regardless of copolymer composition they exhibit nearly the same thermal stability.

A comparison of thermograms of the nonporous model copolymers of NtBA with EDMA and nanoporous copolymers of similar composition, obtained by thermal degradation of poly(A-DitBuU-co-EDMA) (16), is presented in Figure 5. These copolymers show nearly the same thermal stability, thus indicating that nanopores have no significant influence on thermal stability of crosslinked copolymers. It could be attributed to the high degree of crosslinking in both copolymers. Otherwise, nanoporous and nonporous copolymers exhibit different temperature transition behavior. Namely, nanoporous compounds show one phase transition, while corresponding nonporous model copolymers show two phase transitions, as it is evident from Table 3. These results

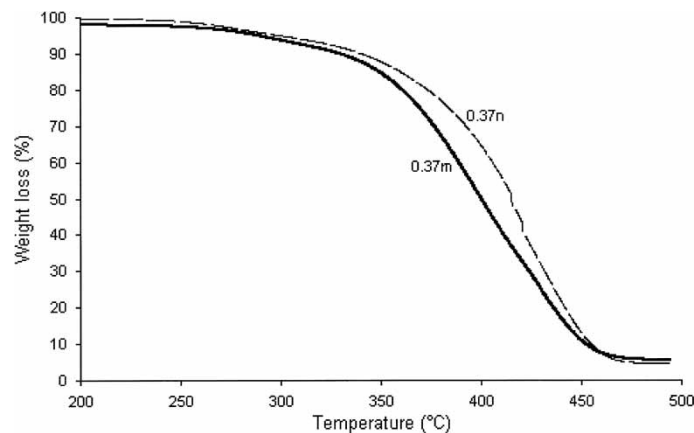


Fig. 5. Thermograms of the nonporous model copolymer of NtBA with EDMA, with NtBA molar ratio of 0.37 m and nanoporous copolymer with NtBA molar ratio of 0.37n.

Table 3. Temperature transitions of poly(NtBA-co-EDMA) nonporous model and nanoporous copolymers

Molar fraction of NtBA in nonporous copolymer ^a (based on N ₂)	Transition temperature (°C) T _g T _{trans}	Molar fraction of NtBA in nanoporous copolymer ^b (based on N ₂)	Transition temperature (°C)
0.22	302; 373	0.18	366
0.37	305; 371	0.37	364
0.57	311; 369	0.55	360
0.65	313; 366	0.64	352

^aPolymerization conditions: 70°C; 2 wt% Bz₂O₂; total monomer concentration 2M/L; in butanone; 48 h; N₂.

^bCopolymers obtained by thermal degradation of poly(A-DitBuU-co-EDMA); in TGA for 5 min at 250°C, in nitrogen (16).

suggest that model compounds have higher structural order than nanoporous copolymers.

Additional information regarding structural differences between nonporous model compounds and nanoporous molecularly imprinted copolymers can be expected from X-ray diffraction and polarized light micrograph analysis. This expectation is based on the previously obtained results regarding structural differences between copolymers of acryl and methacryl cyclohexylamide with ethylene glycol dimethacrylate, having nanoporous and nonporous properties. X-ray diffractograms and polarized light micrographs of imprinted nanoporous copolymers differ from the corresponding model compounds, i.e., imprinted samples show a loss of long-distance order in comparison to model samples (18).

4 Conclusions

Copolymers of NtBA with EDMA were prepared by free-radical solution polymerization using Bz₂O₂ initiator, over a wide composition and conversion range. By performing low-conversion polymerization reactions ($\leq 20\%$), monomer reactivity ratios were determined using the Kelen-Tüdös method and were found to be $r_1(\text{NtBA}) = 0.26$ and $r_2(\text{EDMA}) = 7.05$.

The initial rate of copolymerization decreases with increasing the content of NtBA monomer in the feed. By performing polymerization up to a high conversion (97–100%), nonporous model copolymers of NtBA with EDMA were prepared, and their thermal properties were compared with those of the corresponding nanoporous copolymers which were obtained by thermal degradation of poly(A-DitBuU-co-EDMA) copolymers in TGA experiments. There were no significant differences found in the thermal behavior of those systems. Otherwise, nonporous model poly(NtBA-co-EDMA) exhibit two phase transitions while nanoporous copolymers show one phase transition, thus implying better structural order in nonporous model compounds.

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