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In situ Formation of HEMA-NIPA Compositional Gradients During Polymerization

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Ordered and gradient polymeric materials are very attractive in coating and film technologies. We present here a simple idea to obtain these materials by transferring in one step the well known compositional heterogeneity in time of copolymeric reactions, to a heterogeneity in space. We have obtained ordered materials by sedimenting in a centrifuge insoluble copolymeric chains of 2-hydroxyethylmethacrylate and N-isopropylacrylamide as formed in the precipitant copolymerization. We think that the idea presented here may be extended by other researchers to homogeneous reactions or to network formation.

Keywords: Chain copolymerization, compositional gradient, differential reactivity, acrylics

1 Introduction

Radical copolymerization is an easy and versatile way to obtain copolymers or networks with different properties. In terms of molecular control, unless we carry out the reaction in continuous or azeotropic conditions, differences in co-monomer reactivities lead to an unavoidable compositional heterogeneity along the conversion (1,2). This heterogeneity is therefore intrinsic to the existence of any difference in reactivities. Furthermore, these heterogeneous materials do not exhibit a well controlled molecular order since a mixture of different chains is obtained. However, the object of this paper is to show that this compositional drift along the conversion may also be seen as an opportunity to build special structures during the copolymerization itself (one-step procedure). Here we described the possibility to synthesize so-called gradient materials exhibiting a spatial ordering. These structures may be achieved if we are able to transfer the heterogeneity in time to heterogeneity in space. We will show here that these materials can be obtained for example by precipitating and sedimenting A-B copolymeric chains during their formation starting from a homogeneous solution of the parent monomers.

2 Experimental

2.1 Chemicals

N-isopropylacrylamide, NIPA (ACROS), was recrystallized from an ether/hexane(1:5) mixture. 2-hydroxyethylmethacrylate, HEMA (Sigma), was distilled at reduced pressure. Vitamin C, sodium persulfate and solvents used in this work were purchased from Aldrich and used without further purification.

2.2 Copolymerization

Two reactions have been carried out with a HEMA:NIPA molar ratio of 1:1 and 1:4, respectively ($F_{\text{HEMA}0} = 0.5$ and 0.4 total monomer concentration of 2M). In a cylindrical tube (10 mm diameter), one dissolves the two monomers in water at a concentration of 2M and adds the redox radical initiators (vitamin C, sodium persulfate, 1% weight each). The tubes were then introduced in a centrifuge Eppendorf 5810R where the reaction took place at 40°C and 10000 rpm during 4 h. A *sediment* and *supernatant* were obtained. The residual monomer in the *supernatant* was separated by decantation and allowed to polymerize for a further 18 h. The sedimented polymers were frozen at -20°C and freeze dried overnight. After breaking the cylindrical reaction tubes, we obtained the *sediment* of the samples which was cut into disks of approximately 1–2 mm thickness, labelled as 1, 2, 3 4, 5 and 6 according to its distance from the bottom of the tube and analyzed using an ATR-FTIR together with the copolymer formed from the *supernatant* and labelled as *sup* in Figures 1 and 2.

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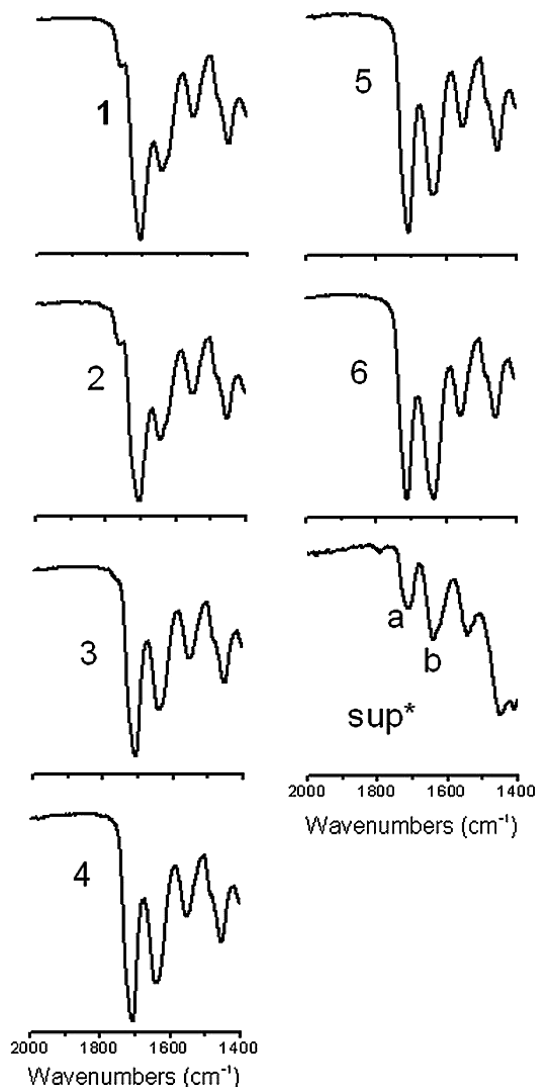


Fig. 1. ATR spectra obtained as described in the Experimental Part for the reaction with $F_{\text{HEMA}0} = 0.5$. Sample **1** corresponds to the bottom part of the sediment, sample **6** to the fraction that has precipitated at the final stage of copolymerization and *sup** to the copolymer formed from residual supernatant. *a* and *b* are the signals used to obtain the copolymer molar fraction.

The weights of the disks were used to obtain conversion data.

2.3 ATR-FTIR

FTIR spectra were registered in a Perkin-Elmer Spectrum One, coupled to an attenuated total reflexion (ATR) device. Four scans were registered with a resolution of 4 cm^{-1} . Spectra of the homopolymers and reference copolymers with initial feed compositions of 0.1, 0.2, ... 0.9 synthesized in a conventional way without the use of a centrifuge were recorded and used to obtain a calibration curve using

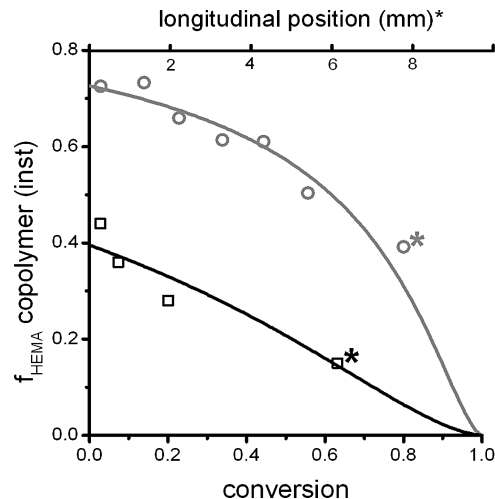


Fig. 2. Experimental HEMA copolymer molar fraction vs. conversion or corrected longitudinal position (to cylindrical shape) for the two reactions (\circ , $F_{\text{HEMA}0} = 0.5$; \square , $F_{\text{HEMA}0} = 0.2$). Reactions were stopped after 4 h and the residual supernatants exhibited the averaged compositions shown in the figure. * = supernatant.

the intensity ratio of the signals at 1706 and 1633 cm^{-1} (I_{1706}/I_{1633}). Details of some spectra are shown in Figure 1.

3 Results and Discussion

The mentioned transfer of the compositional heterogeneity in time in copolymerization reactions to heterogeneity in space has been tried with the precipitant copolymerization of HEMA and NIPA in water at 40°C (above LCST, 3). Under these conditions, the forming copolymers are insoluble in the media no matter their compositions. We have carried out two reactions in a centrifuge (initial HEMA feed molar fractions of 0.5 and 0.2), sedimenting the copolymers *in situ*. This comonomeric pair has also been chosen because they can be considered to exhibit a medium differential reactivity according to literature data of homologous pairs like glycidil methacrylate (GM) and NIPA (4). Virtanen et al. reported a reactivity ratios for this couple of $r_{\text{GM}} = 2.69$ and $r_{\text{NIPA}} = 0.39$ (assuming the reaction to be governed by the terminal model, 5), which may be adequate values to obtain a continuous compositional variation along the conversion, as is shown in Figure 2. In this figure, the theoretical variation of the HEMA instantaneous copolymer molar fraction has been represented as solid lines - for the two mentioned reactions - vs. the conversion using the terminal model (2) and the above mentioned reactivity ratios.

The final sedimented materials were characterized by ATR as described in the Experimental. In Figure 1, the zoomed ATR spectra of the different sample disks from the reaction with $F_{\text{HEMA}0} = 0.5$ are shown as an example

corresponding sample **1** to the fraction that has precipitated first and **6** to the fraction that has been formed at the final stage of the polymerization. We see a continuous variation in the intensity ratios of the C=O signals of the ester and amide functions characteristic of HEMA and NIPA units, respectively. Copolymer compositional data have been calculated using the calibration described in the experimental part, and have been represented vs. the conversion in Figure 2, together with the theoretical lines. According to this Figure, compositional gradients have been formed during the sedimentations, and the experimental data are in good agreement with the theoretical ones.

4 Conclusions

In summary, the compositional heterogeneity of radical copolymerizations may be used as a tool to obtain gradient materials. Copolymerizing a precipitant system in a centrifuge may lead to the creation of compositional order, and therefore can be used for the *in situ* preparation of

gradient materials, as it has been demonstrated here with the HEMA-NIPA copolymeric system.

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