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Copolymerization of Polyurethane Macromer with 2-Hydroxyethyl Methacrylate: NMR Kinetic Study

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Summary

The copolymerization kinetics of polyurethane containing a vinylic bond with 2-hydroxyethyl methacrylate in solution was investigated. The reaction was studied using a JEOL-PS-100 spectrometer at various temperatures and concentration conditions. The a and b exponents in the equation for the overall polymerization rate, $R_p = \text{const}[M]^a[I]^b$ were determined. The reaction products were analyzed by means of ^{1}H-NMR and turbidimetric titration.

Introduction

The presence of a vinyl group in the polyurethane molecule capable of radical polymerization or copolymerization is one of the ways for obtaining products possessing new physical and mechanical properties.

As far as we know, up to the present day only low-molecular weight compounds with the urethane bond have been synthesized, such as α,ω -dimethacryl-(bisethylene glycol)-2,4-toluylenediurethane (LABANA 1968), or some low-molecular weight oligomers derived from it (SPIRIN et al. 1970, GUDZERA et al. 1977). However, owing to the content of two vinyl groups, these compounds give rise to a three-dimensional network in the polymerization or copolymerization already at very low degree of conversion, so that a deeper investigation of the polymerization or copolymerization process is virtually not possible. In spite of this, the copolymerization parameters of the pair dimethacryl-diurethane (mentioned above) with styrene have already been determined (GUDZERA et al. 1976).

A different situation arises if the oligomer based on polyurethane contains only one vinyl group. In such a case no insoluble three-dimensional product is formed, so that it is possible to investigate the copolymerization of such a so-called macromer (macromolecular monomer) with the usual low-molecular weight

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monomer, 2-hydroxyethyl methacrylate (HEMA) in our case, over the whole course of the reaction.

Experimental

Polyurethane based on 4,4´-diphenylmethane diisocyanate and polybutanediol adipate with free isocyanate groups was reacted with 2-hydroxyethyl methacrylate in dimethylformamide solution. The macromer thus obtained contained 7% mol. end bonds (calculated with respect to diphenylmethane units denoted below as R).

The copolymerization reactions were initiated with azobisisobutyronitrile (AIBN) in dimethylformamide d7 solution; the effect of temperature and of the concentrations of monomer, macromer and initiator on the reaction kinetics was investigated.

Experimentally, the copolymerization was carried out directly in a JEOL-PS-100 spectrometer in NMR cells sealed under nitrogen. In this way it was possible to follow the course of copolymerization of any selected time intervals. The integrated band intensities were measured with a built-in integrator with an accuracy of 2%; the temperature stability during measurements was maintained with an accuracy of ±0.5°C by means of JES-VT-3 unit. The absolute temperature values were calibrated using NMR spectra (VAN GEET 1968).

The reaction products were analyzed by means of ^{1}H-NMR and turbidimetric titration. Turbidimetric measurements were performed with a turbidimeter of our own design in a system dimethylformamide (solvent) - di-n-butyl ether (precipitant) in the concentration range 0.003-0.005 g/ml at 30°C.

Results and discussion

The NMR spectra of the reaction mixture recorded in various time intervals at 60°C are shown as an example in Figure 1. The evaluation was carried out using bands in the range τ = 8.7 - 9.05 ppm, due to protons of the methyl groups of HEMA monomeric units which became part of the copolymer. Bands in the range τ = 3.9 - 4.4 ppm and 8.1 ppm respectively are due to protons of CH_2 on the double bond and of CH_3 groups in the monomer. It can be seen in Figure 1 that the integrated intensity of these bands decreases with time, while the integrated intensity of bands in the range τ = 8.7 - 9.05 ppm increases.

The finding that the integrated intensity of bands, I_R, due to aromatic protons of diphenylmethane in the molecule of the macromer (τ = 2.4 - 2.9 ppm) does not change with time during the reaction, was used to establish the internal standard. If r is defined as the molar ratio of monomeric units of HEMA,

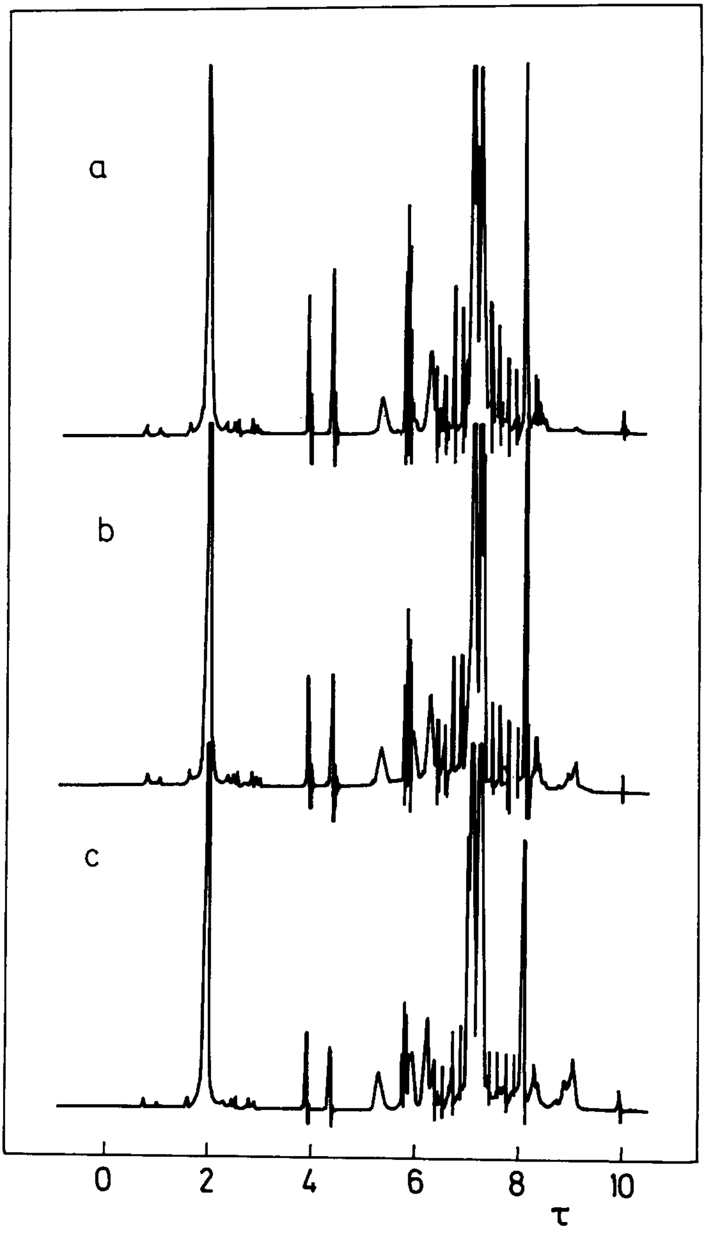

Figure 1. ^{1}H-NMR spectra of the reaction mixture macromer - 2-hydroxyethylmethacrylate in dimethylformamide measured at 100 MHz, 60°C, at a time (a) 7 min (b) 103 min, and (c) 220 min

already reacted and of R units ($r = n_{HEMA}/n_R$), one obtains

$$r = (8/3) I_{CH_3pol}/I_R \qquad (1)$$

where I_{CH_3pol} is the integrated intensity of reacted monomeric units. Using Eq.(1), the time dependences of r on temperature and on the concentration of the individual components were investigated. These dependences of r were linear in all cases within a certain time interval (cf.e.g.Figure 2), and the effective overall copolymerization rate R_p was determined from their slopes

$$R_p = \Delta r/\Delta t \qquad (2)$$

The effect of temperature was investigated on five levels in the range 50-70°C with the other conditions kept constant. The results are summarized in Figure 2. The activation energy of copolymerization of the pair of comonomers under study was determined using the Arrhenius equation and the R_p vs.1/T dependence (cf.Figure 3). The total activation energy E = 87.09 kJ/mol calculated from the slope lies in the range of the usual values (83.7 - 92.1 kJ/mol). Thus, the reaction under study does not differ from other radical polymerization and copolymerization reactions.

The effect of the monomer and initiator concentrations was investigated in the range 0.46 - 1.85 mol HEMA per litre, or 3.6 - 14.6 mmol AIBN/l at 60°C, and the exponents a,b were determined from Eq.(3) for the overall polymerization rate R_p (Figures 4,5)

$$R_p = \mathrm{konst}[M]^a[I]^b \qquad (3)$$

The following values have been obtained: a = 1.0-1.1 and b = 0.457.

Using the above experimental values, it may be said that the copolymerization of the PU-macromer with HEMA proceeds within the range of experimental conditions under study in agreement with the classical kinetic equation. Also, no marked effect of the macromer concentration on the overall copolymerization rate could be determined for the weight ratio PU/HEMA = 0.2 - 1.0.

After reprecipitation into ether, the composition of the reaction products was qualitatively investigated by means of ^{1}H-NMR and turbidimetric titration. Figure 6 shows some typical examples of turbidimetric curves thus obtained. Curve 1 in this Figure relates to the product after reprecipitation. Curve 2 reflects the turbidimetric titration of the product after ex-

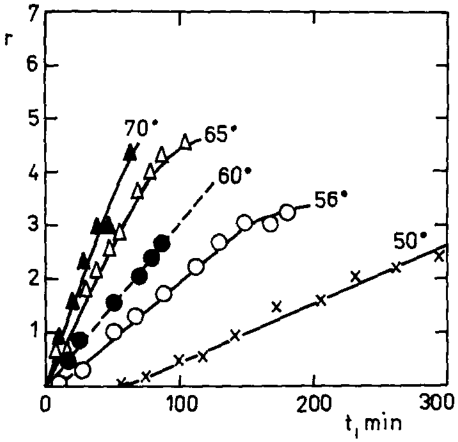

Figure 2. The dependence of r on time at various temperatures, 1% AIBN

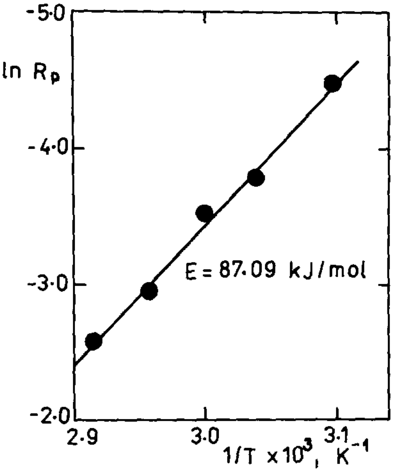

Figure 3. The dependence of ln R_p on 1/T

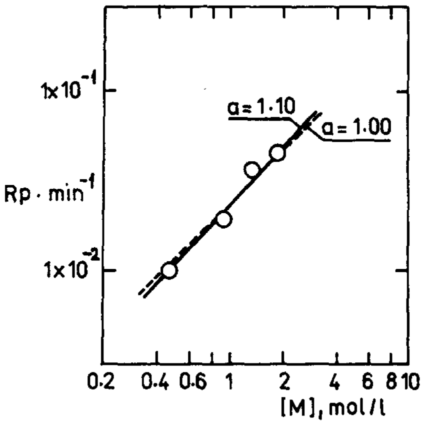

Figure 4. The dependence of R_p on the monomer concentration [M] (60°C, 4.3 mmol AIBN/l)

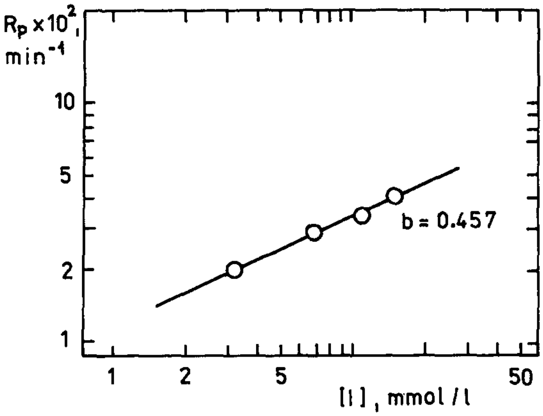

Figure 5. The dependence of R_p on the initiator concentration (60°C, monomer concentration 0.925 mol/l)

traction with methanol, which is a good solvent for the homopolymer of 2-hydroxyethyl methacrylate and a precipitant for polyurethane. Curve 3 shows the course of titration of the methanolic extract after

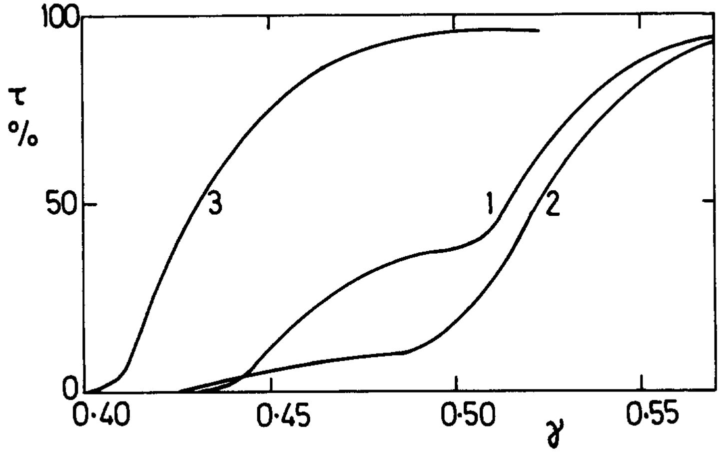

Figure 6. Turbidimetric curves (1) of reaction product, (2) of extracted product and (3) of extract.
τ - turbidity, where 0% is a value for pure solvent and 100% corresponds to wholly precipitated polymer, γ - is the volume fraction of precipitant (di-n-butyl ether) in the system

drying. Two distinct waves can be seen in curve 1, where the precipitation threshold of the second wave corresponds to the pure initial macromer. The precipitation threshold of curve 3 coincides with the value measured for poly(2-hydroxyethyl methacrylate).

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