Polymer Bulletin 34, 509–514 (1995)

Polymer Bulletin

Synthesis and polymerization of unsaturated monomers with OH groups in their structure: 2-(hydroxyethyleneoxyterephthaloyloxy) ethyl acrylate

J. Guzmán, E. Riande

Instituto de Polímeros, C.S.I.C., Juan de la Cierva, 3, E-28006-Madrid, Spain

Received: 20 December 1994/Accepted: 10 January 1995

Summary.

The synthesis and polymerization of new unsaturated monomers derived from acrylic acid and an aliphatic-aromatic glycol is reported. Values of $k_p/k_t^{1/2}$ were obtained for the monoacrylate monomer and compared with those found for other acrylic monomers. The thermal properties of the starting glycol (Bis[2-hydroxyethyl]terephthalate), monomers (monoacrylate and diacrylate) and linear polymer were determined by calorimetric techniques. The results show the influence of intermolecular interactions (hydrogen bondings) on these properties.

Introduction

The development of new polymers containing hydroxyl groups in their structure and the study of their properties is an important subject of research in Polymer Science owing to the particular characteristics of this kind of polymers (1-8). In connection with this, efforts have been devoted in our laboratories to the synthesis, kinetics of polymerization and properties of different polymers derived from polyalcohols with different structures. These studies are interesting to obtain an adequate information about the influence of hydrophilic side groups on the properties of acrylic and methacrylic polymers.

Up to date, we have synthesized acrylic and methacrylic ester monomers and their corresponding polymers with only aliphatic and cycloaliphatic groups (9-11)incorporated in the side groups. In this work, the synthesis and polymerization of a hydroxylated monomer with aromatic groups in the pendent chain is reported. In addition, the thermal properties of both the monomer and the polymer are investigated.

Experimental Section

Materials

Bis[2-hydroxyethyl]terephthalate (BHET) was synthesized from dimethylterephthalate (1 mole) and ethylenglycol (6 moles) by direct transesterification with isopropyl titanate as catalyst. The reaction was carried out at 175°C for seven hours until practically all the methanol was evolved. The crude product was precipitated in distilled water and purified by crystallization from a mixture of acetone/n-hexane (m.p. 114°C). Toluene, chloroform and Dioxane (Merck) were purified by conventional methods whereas acryloyl chloride (Fluka) and triethylamine were used as received. 2,2'-Azobisisobutyronitrile was purified by crystallization in methanol and dried under high vacuum at room temperature.

Synthesis of the 2-(hydroxyethyleneoxyterephthaloyloxy) ethyl acrylate (HETA).

The synthesis of HETA was carried by reaction between BHET and acryloyl chloride at 20°C in benzene under nitrogen atmosphere using triethylamine to neutralize hydrogen chloride evolved during the reaction. The mole ratio between the glycol and the acid chloride was 7/3 in order to obtain about 80% of the monosubstituted compound (9). Acryloyl chloride was slowly added to the mixture over two hours and the reaction proceeded for four hours more. The triethylamine salt was removed by filtration and further by several extractions with distilled water. The reaction mixture was then dried by addition of anhydrous sodium sulfate, filtrated and the solvent evaporated. To separate the excess of HETA, the crude product was dissolved in toluene and the BHET was crystallized from the solution at 0°C for 24 hours. The solvent was finally eliminated from the mixture of monomers (mono and diacrylate) by evaporation under vacuum.

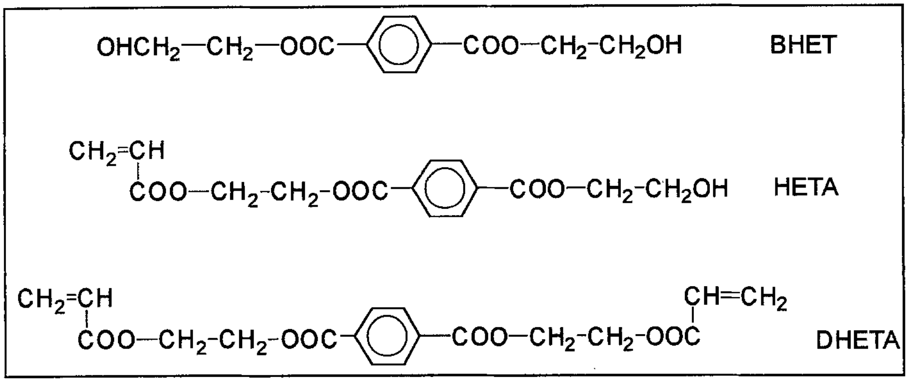
Separation of the mixture of monomers.

Owing to the difficulty involved in the separation of monomers by distillation, flash chromatography was used for the purification. The separation was carried out in a column of silica (230-400 mesh ASTM) using an 80/20 mixture of toluene/ethyl acetate as eluent. HETA was extracted from the column by successive separations of the diacrylate and final elution with pure ethyl acetate.

Characterization of the monomers.

The two monomers obtained in the reaction (HETA and the diacrylate (DHETA)) were characterized by ^{1}H and ^{13}C NMR spectroscopy and HPLC. The purity of the two monomers was found to be higher than 99%. NMR spectra of these compounds were obtained with a Varian XL-300 operating at 300 MHz for ^{1}H and 75.4 MHz for ^{13}C using deuterated chloroform as solvent and tetramethylsilane as internal reference.

The monomers are crystalline solids which do not crystallize from the melt after long periods of time. Their melting points were determined calorimetrically with a Perkin-Elmer DSC8 calorimeter at a heating rate of 10°C/min. The glass transition temperatures of the amorphous monomers were also measured by DSC at the same heating rate; previously, the monomers were melted at a temperature 30°C higher than their melting points and rapidly cooled in liquid nitrogen.



Polymerization reactions

The polymerization of HETA was carried out in dioxane solution at 50 and 65°C using AIBN as initiator. The concentrations of monomer and initiator were, respectively, 0.4 and 5.6×10^{-3} mole L^{-1}. The progress of the reaction was measured with a double branch dilatometer with 6.5 cc volume and 1.06 mm capillary diameter.

Characterization of the polymer.

The polymer was isolated from the reaction medium by several precipitations in cold n-hexane and finally it was purified by freeze drying from dioxane solutions. The characterization of the purified product was done with ^{1}H and ^{13}C NMR spectroscopy using a Varian XL 300, deuterated chloroform as solvent and tetramethylsylane as internal standard. The glass transition temperature of the polymer was determined calorimetrically using the same conditions indicated above for the monomers.

Results and discussion.

Thermal Properties

The melting points of the monomers as well as their enthalpies and entropies of fusion are given in Table 1 where the corresponding values for the starting glycol BHET are also included. As can be seen, both the melting points and the entropies of fusion of the monoacrylate are intermediate to those of the other compounds, whereas the lowest value is found for the enthalpy of fusion. In the same table the glass transition temperatures (Tg) of the three compounds are also shown. The higher Tg corresponds to the BHET, whereas the lower value is obtained for the diacrylate. This fact may be attributted to the presence of OH groups in BHET and in the monoacrylate that may increase the intermolecular interactions through hydrogen bridges.

The fact that the polymer exhibits a rather low glass transition temperature (271°K) indicates that in spite of the size of side groups, the polymer has a relatively high flexibility.

Compound	T_m ,°K	ΔH_m Kcal/mol	ΔS_mCal/°Kmol	T_g, °K
BHET	387	9.07	23.4	242
HETA	317.5	8.08	25.4	220
HETDA	362	10.8	29.8	217
PHETA				271

Table 1.Melting temperatures (T_m), enthalpies and entropies of fusion (ΔH_m and ΔS_m) and glass transition temperatures (T_g) for the monomers and the polymer.

Kinetics of polymerization.

By assuming that the decomposition of the initiator is a first order reaction, the rate of radical initiated polymerization can be written as:

$$-\frac{dM}{dt} = k_p\left(\frac{2fk_d[I_o]}{k_t}\right)^{1/2}[M]\exp\left(\frac{-k_dt}{2}\right) \qquad (1)$$

where k_d, k_p and k_t are the rate constants for initiator decomposition, propagation and termination reactions, respectively, [M] is the instantaneous concentration of the monomer, $[I_o]$ is the initial concentration of the initiator, and f is the efficiency of the initiator. The integration of equation 1 gives:

$$\ln\frac{[M_o]}{[M]} = 2k_p\left(\frac{2f[I_o])}{k_tk_d}\right)^{1/2}\left[1-\exp\left(\frac{-k_dt}{2}\right)\right] = \frac{k_p}{k_t^{1/2}}Z \qquad (2)$$

Dilatometric techniques (9) were used to obtain kinetic data and to determine the kinetic constants. The experimental results are represented according to equation 2 in Figure 1.

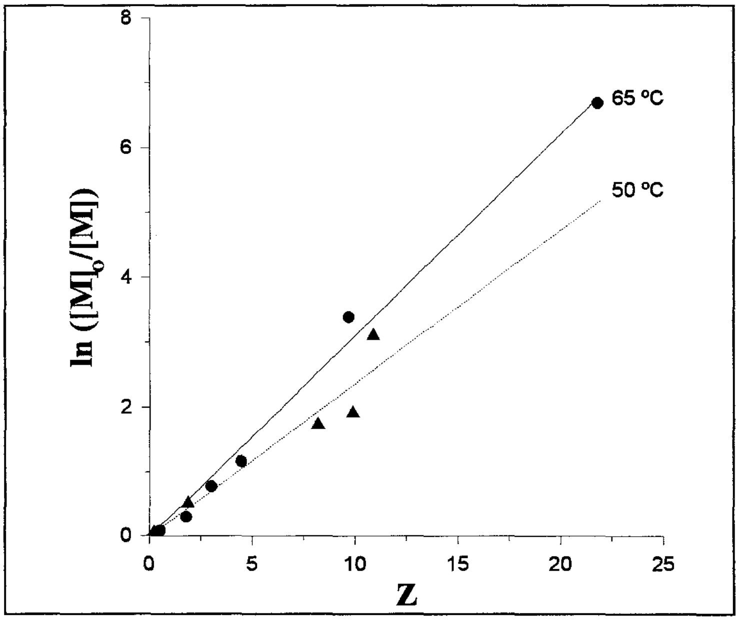


Figure 1. Linear plots according to equation 2 for the polymerization of HETA in 1,4-Dioxane at 50 °C and 65 °C.

The values of k_d at the two temperatures were taken from the literature (12,13) and by considering the efficiency of the initiator f=0.6, values of $k_p/k_t^{1/2}$ of 0.23 and 0.31 $l^{1/2}$ $mol^{-1/2}s^{-1/2}$ were obtained at 50 and 65°C, respectively.

The comparison between the kinetics of polymerization of HETA and that of other acrylates suggests that low values of $k_p/k_t^{1/2}$ are obtained for the first monomer. Probably, high steric hindrances caused by the bulky substituent will decrease more k_p than k_t, the contrary that habitually occurs in the case of the polymerization of other methacrylic and acrylic esters (10).

References.

1. Kusi R. P, Turner D. T (1974) J. Dent. Res. 53:948
2. Kaetsu I, Yoshida K, Okubo H (1979) J. Appl. Polym. Sci. 24: 1515
3. Okubo H, Yoshida K, Kaetsu I (1979) Int. J. Appl. Radiat. Isot. 30: 209
4. Duncan R, Kopecek J (1984) Adv. Polym. Sci. 57: 51.
5. Payne M.S, Horbett T.A (1987) J. Biomat. Res. 21: 843
6. Brannon-Peppas L, Peppas N.A (1990) Biomaterials 11: 635
7. Wen S, Yin X , Stevenson W.T.K (1991) J. Appl. Polym. Sci. 43: 205.
8. Sefton M.V, Stevenson W. T. K (1993) Adv. Polym. Sci. 107:143
9.Iglesias M.T, Guzmán J, Riande E (1994) J. Polym. Sci. 32:2565
10.Iglesias M.T, Guzmán J, Riande E (1995) J. Polym. Sci. (in press)
11.Guzmán J, García F, de la Peña J.L, Riande E (unpublished results)
12 Van Hook J.P , Tobolsky A.V (1958) J.Am. Chem. Soc. 80: 779
13.Tulig T.J, Tirrel M (1982) Macromolecules 15: 459
14. Brandrup J, Immergut E.H(ed) Polymer Handbook 2nd .Ed, Wiley, New York 1975

Acknowledgments.

We gratefully acknowledge the skilful technical assistance of Mr. D. Delgado and the finantial support of the CICYT through the grant PB-92-0773