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Synthesis of Block Copolymers by Combination of an Activated Monomer and Free Radical Polymerization Mechanism

Yusuf Yagci* **and I. Ersin Serhatli**

Department of Chemistry, Istanbul Technical University, Maslak-Istanbul 80626, Turkey

Przemyslaw Kubisa and Tadeusz Biedron

Center of Molecular and Macromolecular Studies, Polish Academy of Science,
90-362, Boczna 5, Poland

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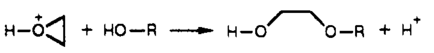
ABSTRACT: Epichlorohydrin (ECH) was polymerized by an activated monomer mechanism (AM) in the presence of 4,4′-azobis(4-cyanopentanol). Spectroscopic and degradation studies showed that polymers obtained via this initiation method contained an azo linkage in the main chain. These prepolymers were employed in the polymerization of styrene (St) to yield block copolymers.

Introduction

Block copolymers have recently been a subject of interest mainly from the practical viewpoint of material science. Block copolymers may exhibit diverse mechanical properties which are not shown by homopolymers. Synthesis of block copolymers having different combinations of components and molecular weight distributions has been a subject of interest for many years. Classical methods using a single type of propagating species such as anionic polymerization are limited to certain types of monomers and exclude monomers that polymerize by other mechanisms. The transformation approach in block copolymer synthesis, in which different propagating species are used, allows multiple combinations of monomers.[1,2] In our preceding papers, we used the transformation approach to demonstrate the possibility of producing block copolymers by combinations of free radical polymerization with anionic insertion,[3] cationic,[4-8] promoted cationic,[9] redox,[10-13] photoinitiated free radical,[14-17] and condensation[18-22] polymerizations. In these processes functional azo initiators were used as polymerization transformation agents.

The cationic polymerization of oxiranes may proceed in the presence of hydroxyl group containing compounds by the activated monomer (AM) mechanism,[23-26] which may be represented generally as follows:



(1)

Thus, the propagation involves the reaction of a protonated (activated) monomer molecule with a nucleophilic site in the neutral growing macromolecule. AM polymerization offers several synthetic possibilities including linear telechelics and macromonomers.[26]

In the present work, an azoinitiator bearing hydroxyl end groups was used in the AM polymerization of epichlorohydrin to produce polymers with an azo linkage in the main chain. Thermolysis of these polymers in the presence of vinyl monomers makes it possible to synthesize block copolymers of differential chemical nature.

Experimental Section

Materials. 4,4′-Azobis(4-cyanopentanol) (ACP) was synthesized according to the described procedure.[27] Styrene (St) was purified by conventional drying and distillation procedures. Diethyl allylmalonate was used without further purification. Epichlorohydrin (ECH) was purified by fractional distillation. The middle fraction (80 vol %) was collected (bp = 116 °C at 760 mmHg, $n^{20}{}_{D}$ = 1.4380, purity 99.5% by GLC).

Activated Monomer Polymerization of ECH. ECH (2.0 g, 2.17×10^{-2} mol) was added dropwise (0.1 g/h) to a solution of 0.147 g (5.83×10^{-4} mol) of ACP containing 0.01 g of BF_3·THF complex in 4 mL of $CHCl_3$. After addition of ECH the solution was kept at room temperature for an additional 24 h. The product was washed with water to remove the catalyst and dried under vacuum after evaporating the solvent. A viscous liquid was obtained (0.727 g, 28% yield of ECH).

Thermolysis of PECH. The thermal degradation of PECH was carried out in methylene chloride solution containing a given amount of diethyl allylmalonate as a radical terminator. Degassed solutions were heated at 70 °C. At end of 2 h, molecular weights were measured.

Block Copolymerization. An appropriate solution of the above-obtained PECH and St were placed in Pyrex tubes. The mixture was degassed in the usual manner prior to heating at 70

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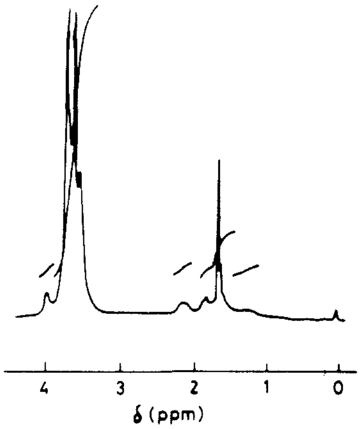


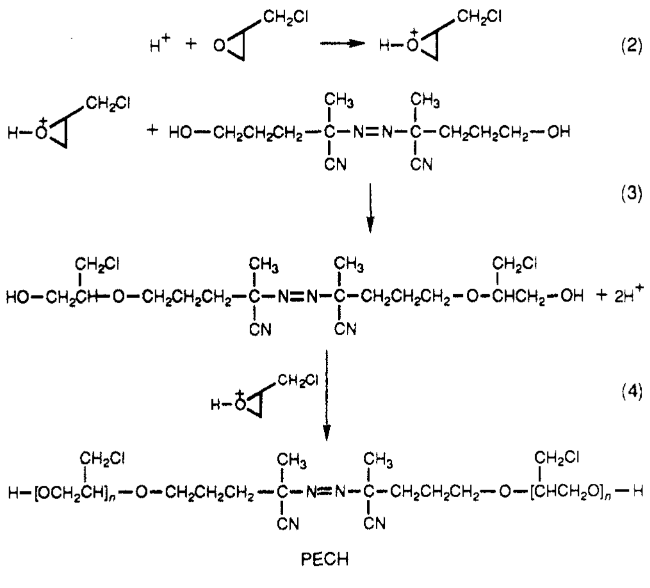
Figure 1. ^{1}H NMR spectrum of PECH with an azo linkage.

°C in a thermostated bath. At the end of 150 min, polymer was obtained from the reaction mixture by precipitation into methanol.

Analysis. GPC chromatograms were obtained by using a Knauer M64 with tetrahydrofuran as the eluent and a flow rate of 1 mL min^{-1}. Molecular weights were calculated by reference to polystyrene standards. ^{1}H NMR spectra were taken on a Bruker 200 spectrometer in $CDCl_3$ with tetramethylsilane as the internal standard. IR spectra were recorded on a Shimadzu Model IR-400 spectrophotometer on KBr disks. DSC measurement was made on a Rigaku Model DSC 8230 B instrument.

Results and Discussion

ECH was polymerized efficiently using 4,4'-azobis(4-cyanopentanol) as a hydroxyl-containing compound by the AM polymerization mechanism according to the following reactions:



Polymerization was conducted under typical conditions, i.e., by slow addition of ECH to a solution of initiator containing catalyst. Reaction was considerably slower than in the presence of simple diols (e.g., ethylene glycol (EG)), and only 28% conversion was obtained under conditions sufficient to reach complete conversion in the polymerization initiated with EG. From the initial concentrations and conversion, the expected DP$_n$ can be calculated as equal to 10.4, which corresponds to M_n = 1180.

Figure 1 shows the ^{1}H NMR spectrum of the product in $CDCl_3$ solvent. The spectrum yields an M_n that is in agreement with the M_n obtained from GPC measurements (M_n = 1500); the five protons of the ECH repeating units appear in the 3.6–3.8 ppm region. At 4.0 ppm the signal of the HOCH terminal units is present (the content of primary hydroxyl end groups in the AM polymerization of ECH is below 5 mol %). The signals of the CH_3 and CH_2 groups of the azoinitiator moiety appear between 1.7 and 2.3 ppm. The integration ratios agree within ±15% with the structure shown in reaction 4 with an average n of 5. Further evidence for the presence of the azo linkage was obtained from the thermal degradation of polymers produced by means of AM polymerization. As can be seen from the GPC chromatograms in Figure 2, after thermolysis of PECH in methylene chloride in the presence of diethyl allylmalonate at 70 °C, a significant reduction in the molecular weight was observed. The number of chain scissions per macromolecule, $N_s = (M_{n0}/M_{n1}) - 1$, is found to be about 0.6, where M_{n0}(2200) and M_{n1}(1400) denotes the number-average molecular weight of PECH before and after thermolysis, respectively. The decomposition kinetics of PECH were studied by DSC according to Nuyken's method.[28] The activation energy for the decomposition was estimated to be 120 kJ mol^{-1} from the DSC trace (Figure 3) as measured in a solvent-free system, which is in good agreement with the reported value for polymeric azoinitiators.[20]

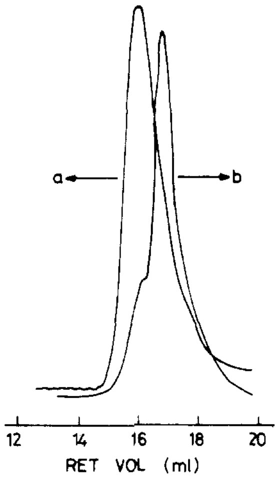
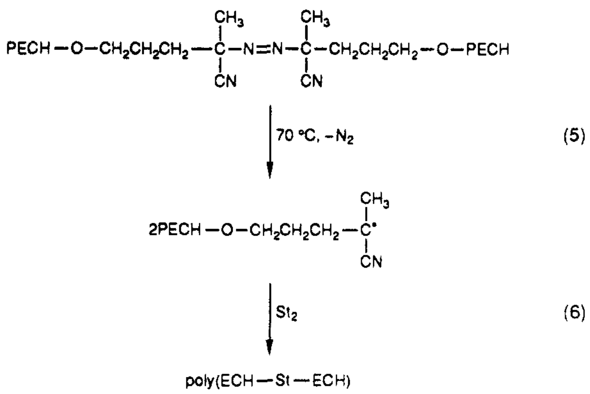


Figure 2. GPC traces for PECH (a) before and (b) after thermolysis.

PECH having an azo linkage was used in the polymerization of styrene (St). A solution of St (7.7 mol L^{-1}) in methylene chloride containing 57 g L^{-1} PECH was heated at 70 °C for 2 h to produce a block copolymer of St and EPCH with a yield corresponding to 12.5% conversion of St.



A control control experiment under similar experimental conditions without PECH produced very little polymer after the same reaction time. By GPC analysis, the formation of block copolymer was evident as shown in

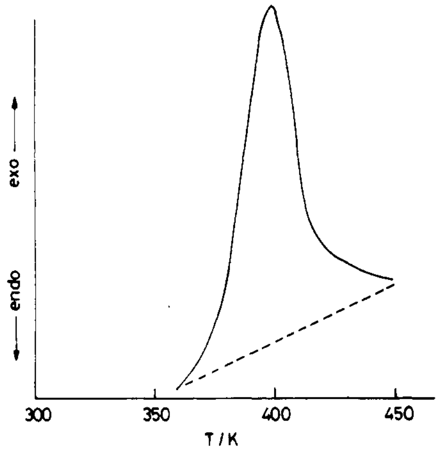


Figure 3. DSC thermogram of ECH with an azo linkage; heating rate 10 °C min^{-1} under a nitrogen flow.

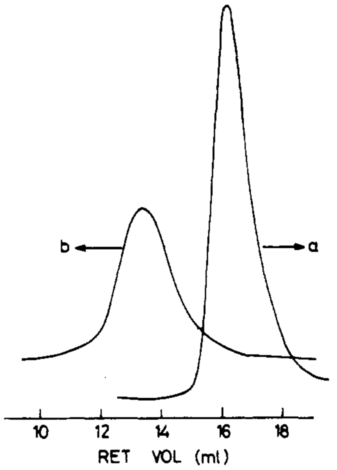


Figure 4. GPC traces for (a) PECH with an azo linkage (M_n = 2200) and (b) the block copolymer of ECH and St (M_n = 29 200).

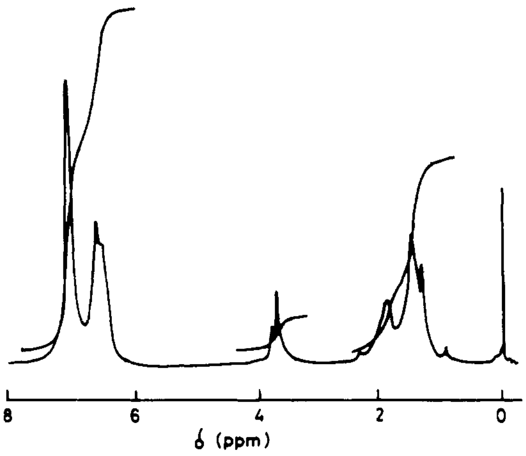


Figure 5. ^{1}H NMR spectrum of the block copolymer of St and ECH.

Figure 4, where GPC traces recorded with the prepolymer (PECH) and block copolymer are shown. The chromatogram of the block copolymer shows a unimodal molecular weight distribution and does not possess a peak at high elution volume corresponding to unreacted PECH. Dual GPC detection by refractive index and ultraviolet recording allowed a clear assignment of the block copolymer formation, as homo-PECH is transparent at the wavelength (254 nm) of the UV detector. The block copolymer structure was also assigned by means of spectral measurements. The IR spectrum of the block copolymer shows the characteristic bands of both St and ECH segments. The NMR spectrum of the copolymer (Figure 5) displays signals at 1.2–2.0 ($\mathrm{CH_2}$ and CH of St segments), 3.55–3.8 ($\mathrm{CH_2}$, $\mathrm{CH_2Cl}$, and CH protons of ECH segments), and 6.5–7.3 ppm ($\mathrm{C_6H_5}$ of St segments). The NMR spectrum appears to have a St/ECH ratio of about 10:1. This value agrees with that obtained from GPC measurements (10.6: 1). The type of the block copolymer greatly depends on the kinetic behavior of the particular monomer involved.

Initiation of St polymerization by means of azo-linked PECH is expected to yield PSt molecules with a PECH unit at each end since termination occurs by radical–radical combination.[29]

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