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Photoactive polyepichlorohydrin:

1. Synthesis of polyepichlorohydrin with terminal benzoin groups by activated monomer polymerization

Yusuf Yağcı[1], Yeşim Hepuzer[1], Ayşen Önen[1], İ. Ersin Serhatlı[1], Przmylaw Kubisa[2], and Tadeusz Biedron[2]

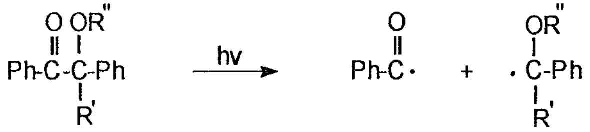
[1]Istanbul Technical University, Department of Chemistry, Maslak 80626, Istanbul, Turkey
[2]Center of Molecular and Macromolecular Studies, Polish Academy of Science,
PL-90362 Boczna 5, Poland

Summary

Epichlorohydrin (ECH) was polymerized by an activated monomer mechanism (AM) in the presence of benzoin (B) and α-methylol benzoinmethylether (MBME), respectively. Spectroscopic studies showed that polymers obtained via this initiation method contained benzoin terminal groups.

Introduction

Benzoin and derivatives are frequently used as photoinitiators for vinyl polymerization [1]. Upon irradiation, these compounds undergo α-cleavage yielding benzoyl and substituted benzyl radicals.



$$\mathrm{Ph{-}C(=O){-}C(OR'')(R'){-}Ph} \xrightarrow{h\nu} \mathrm{Ph{-}\dot{C}{=}O} + \mathrm{\cdot C(OR'')(R'){-}Ph}$$

R' = H, alkyl, substituted alkyl
R'' = H, alkyl, substituted alkyl

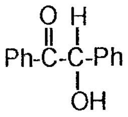
Both radicals are capable of initiating vinyl polymerization [2]. However, they may exhibit different reactivities and roles if the radical and monomer concentrations are varied. Monomer structure also influences the reactivity.

The attachment of structurally related benzoin and its derivatives to the polymer main and side chains would afford a convenient procedure for block and graft copolymer formation, respectively. We have recently reported [3,4] the synthesis of polymers containing photoactive benzoin terminal groups using azobenzoin initiators. These prepolymers were successfully employed [5] in the preparation of block copolymers.

It has been shown that oxiranes can be polymerized in the presence of hydroxyl containing compounds by the activated monomer (AM) mechanism [6,7]. The propagation in these systems can be represented by the following reaction;

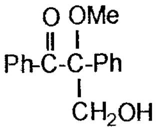
By its nature, this process may be adapted so that hydroxy group containing functional molecules, monomers and polymers are used as initiators to yield telechelic, macromonomer and block copolymers, respectively [7]. We have recently synthesized block copolymers by combination of AM and free radical polymerization mechanism [9]. In the first stage polyepichlorohydrin (PECH) containing a central azo linkage have been synthesized by use of a functional initiator in AM polymerization. This central linkage is then decomposed in the presence of a comonomer to give block copolymers.

In the present work, the following benzoin type photoinitiators were used in the AM polymerization of epichlorohydrin (ECH) to produce polymers with terminal photoactive groups.



$\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}{-}Ph}$

(B)



$\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{CH_2OH}{|}}{\overset{\overset{OMe}{|}}{C}}{-}Ph}$

(MBME)

Experimental

Materials

Benzoin (B) (Aldrich) was used without further purification. α-Methylol benzoin methyl ether (MBME) was purified according to the described procedure [10]. Epichlorohydrin (ECH) was purified by fractional distillation. The middle fraction (80 vol %) was collected (bp=116^{0}C at 760 mm Hg, n_D=1.438 purity 99.5 % by GLC).

Polymerization Procedure

1.14 g (5.38 x 10^{-3} mol) of B was dissolved in 4 ml of methylene chloride and 0.2 ml of BF_3 THF complex was added.

To this solution 14.7 g (0.162 mol) of ECH was added dropwise within 48 hours, with constant stirring, at room temperature. At the end of this period, the viscous liquid was washed with 5 % aqeous $NaHCO_3$ in order to neutralise the catalyst and subsequently with three portions of methanol to remove traces of unreacted initiator and low molecular weight (presumably cyclic) ECH oligomers, if present. Isolated polymer was dried on the vacuum line at room temperature for 24 hours.

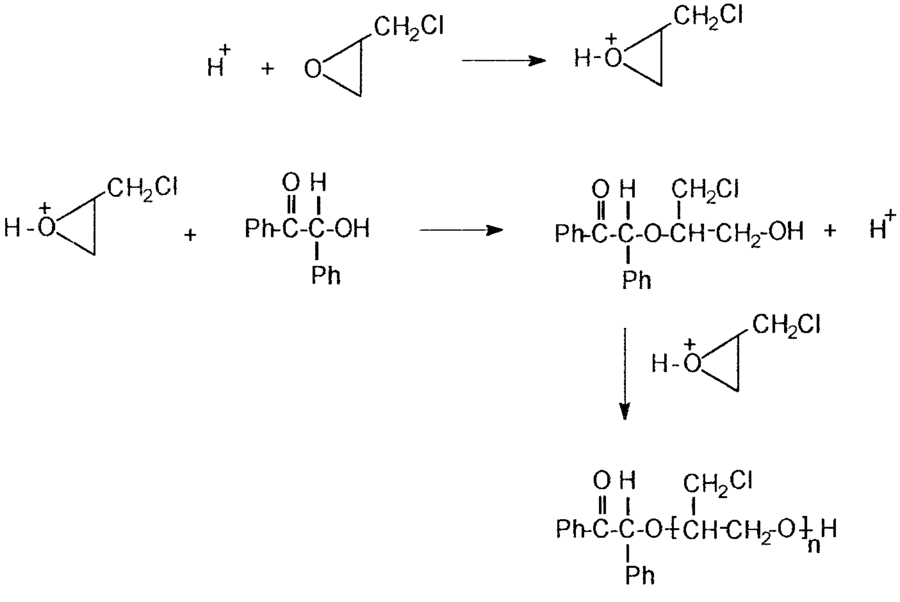
The same procedure was used for polymerization with substituted benzoin (MBME) as initiator.

Analysis

GPC chromatograms were obtained by using LKB 2150 HPLC chromatograph with the set of 4 columns: 1000, 500, 100 and 100 A. THF was used as the eluent, the reported curves were obtained with RI and UV detection. ^{1}H-NMR spectra were recorded using Bruker 200 AC spectrometer, in $CDCl_3$ solution with tetramethylsilane as the internal standard. UV spectra were recorded with Hewlett Packard 8452 A spectrophotometer.

Results and Discussion

Benzoin (B) and α-methylol-benzoinmethylether (MBME) were used as initiators of AM polymerization of ECH catalysed with BF_3 THF complex.



PECH

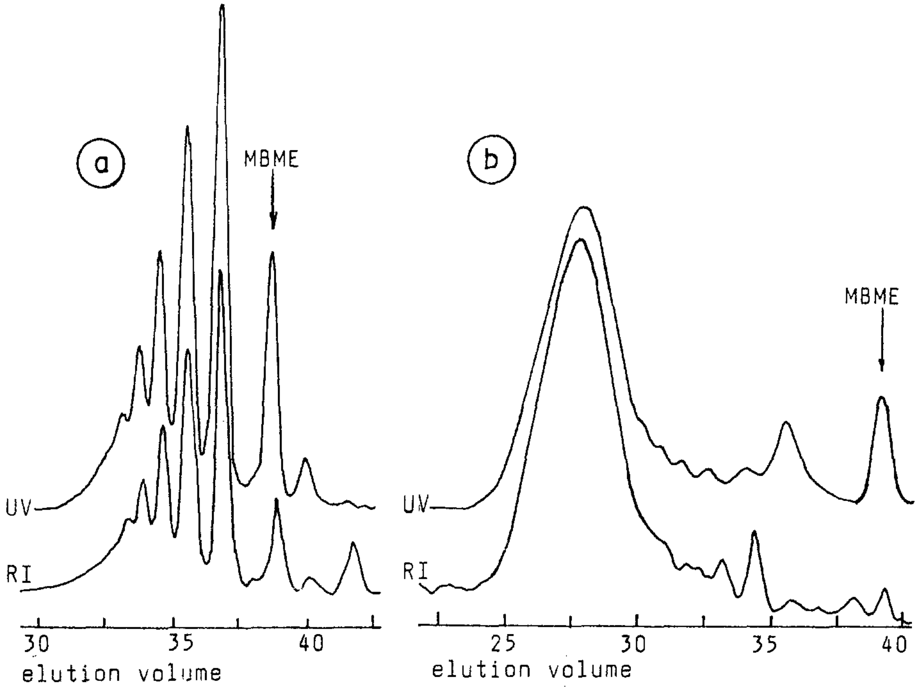


Figure 1. Gel permeation chromatograms of the reaction mixture (with MBME as initiator) at different conversions.
(a) [ECH] added/$[MBME]_0$ = 5, (b) [ECH] added/$[MBME]_0$= 25.

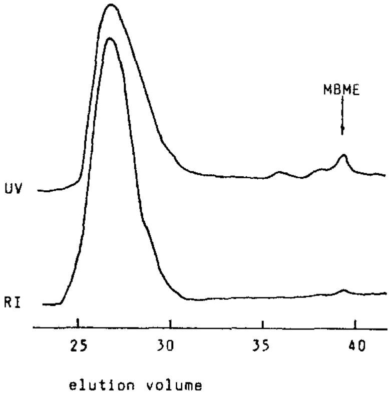


Figure 2. Gel permeation chromatogram of the isolated and purified (by washing with methanol) product of the polymerization (with MBME as initiator) by UV and RI dedection.

In both cases reaction was carried out by slow addition of ECH to the solution of B or MBME in methylene chloride, in the presence of the catalyst. At these conditions, both initiators were consumed at the early stages of the reaction, as evidenced by the decrease of corresponding signals in GPC chromatograms of the reaction mixtures at different conversions (Fig.1). After termination of the polymerization the products (viscous liquids) were extracted with methanol in order to remove the possibly present traces of unreacted initiators. The GPC curve for purified product is shown in Fig.2.

The products were analysed by ^{1}H-NMR and UV spectroscopy. In ^{1}H-NMR spectra, the group of signals at 3.5-3.8 ppm, corresponding to CH_2, CH and CH_2Cl groups of the PECH chain appears, together wit a signals in the range of 7.2-7.5 ppm, corresponding to aromatic protons in benzoin moiety (end group). Additionally, for the products prepared with MBME as initiator (BME-PECH), the singlet at 3.36 ppm appears. As this signal is absent in the spectra of polymers prepared with B as initiator (B-PECH), it was assigned to CH_3O group in the incorporated MBME moiety.

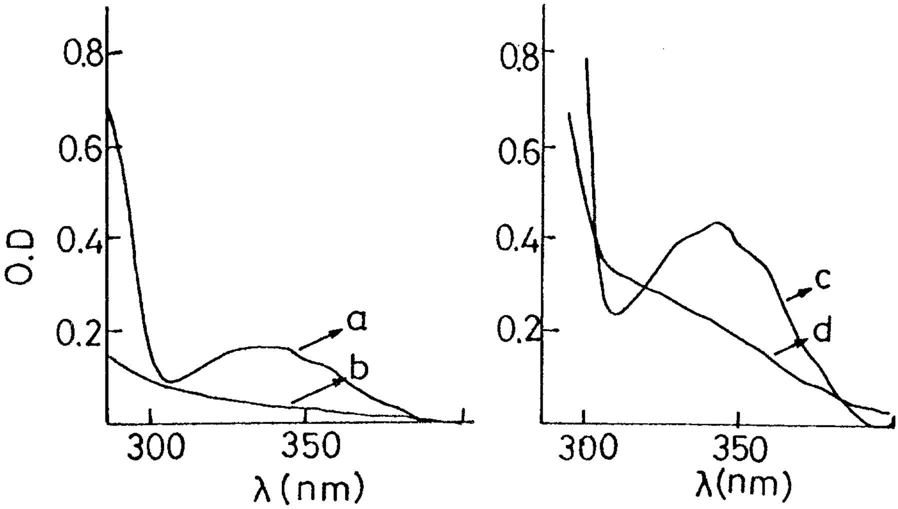


Figure 3. UV absorption spectra of methylene choride solutions containing (a) B (6.6×10^{-4} mol l^{-1}), (b) B-PECH (1.33 g l^{-1}), (c) MBME (2.3×10^{-3} mol l^{-1}) and (d) MBME-PECH (2.03 g l^{-1})

In the UV analysis (Fig.3), the spectra of initiators were recorded as reference. In the UV spectrum of BME-PECH, absorption band at 340 nm ($\varepsilon = 2.05 \times 10^2$ mol^{-1} l cm^{-1}) corresponding to $n \rightarrow \pi^*$ appears together with a much stronger absorption with a maximum at 250 nm. In the spectrum of B-PECH only the slight shoulder is observed at 340 nm and the extinction coefficient measured at 340 nm is considerably lower ($\varepsilon = 0.93 \times 10^2$ mol^{-1} l cm^{-1}). These values were consequently used to calculate the content of aromatic end groups in polymers.

Further studies on the use these polymers as photoinitiators are now in progress and will be published elsewhere.

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