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SYNTHESIS OF EPICHLOROHYDRIN-METHYL METHACRYLATE BLOCK COPOLYMERS VIA ACTIVATED MONOMER-TO-PHOTO INITIATED FREE RADICAL MECHANISM

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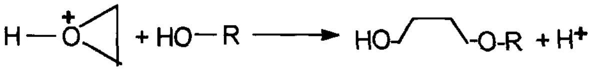
ABSTRACT

Epiclorohydrin(ECH) was polymerized by an activated monomer mechanism (AM) in the presence of N,N'-diethyl-N,N'-bis(2-hydroxy ethyl) thiuram disulfide(DHTD). Poly(epichlorohydrin) (PECH) possessing thiuram disulfide group in the main chain thus obtained was used in the photo induced polymerization of methyl methacrylate to yield PECH-PMMA block copolymers. Characterization of block copolymers was carried out by spectroscopic methods.

INTRODUCTION

In the synthesis of block copolymers, combination of polymerization types has been used successfully [1]. This requires switching the mode of polymerization employed for the first monomer to a different mode most suitable for polymerizing second monomer[2]. The transformation approach in the block copolymer synthesis, in which different propagating species areused, allows multiple combinations of monomers[3]. Previously, it was reported the synthesis of block copolymers cationic and radical[4-5], anionic and radical[6-7], Redox and thermal radical[8-11], thermal radical and photochemical[12-13], activated monomer and radical routes[2].

The cationic polymerization of oxiranes may proceed in the presence of hydroxyl group containing compounds by the activated monomer mechanism(AM)[14-19] which may be represented generally as follows:



Thus the propagation involves the reaction of protonated(activated) monomer molecules with a nucleophilic site in a neutral growing macromolecule.

In the present work, a photo initiator bearing hydroxyl end group was used in the AM polymerization of ECH to produce polymers with a thiuram disulfide linkage in the main chain. Photolysis of these polymers in the presence of vinyl monomers makes it possible to synthesize to block copolymers of different chemical nature.

EXPERIMENTAL

Materials:

ECH (Merck) was purified by fractional distillation. Middle fraction was collected and used without further purification. 57 % Tetrafluoroboric acid solution in diethyl ether was used as purchased. MMA was purified and distilled by conventional manner.

Synthesis of DHTD:

DHTD was prepared by the reaction of 2-ethylamino ethanol, CS_2 and I_2 in $CHCl_3$ according to the method reported in the literature[20]. IR($CHCl_3$): 3350(-OH), 2950(-CH_2-), 1360(-C-N), 1050 (C=S), 650(-C-Cl).

Activated monomer polymerization of ECH:

ECH(9.4 g, 0.10 mol) was added dropwise to solution 0.19 g (5.8 10^{-4}mol) of DHTD containing 0.5 ml HBF_4 in 20 ml of CH_2Cl_2 at 0 °C. 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 (5.3 g, 56 % yield of ECH).
IR(CHCl3): 3500(-OH), 2900(-CH2-), 1750 and 1650(-CH2-)bending 1345(-C-N), 1070(-C=S), 650-780(C-Cl).

Block copolymerization:

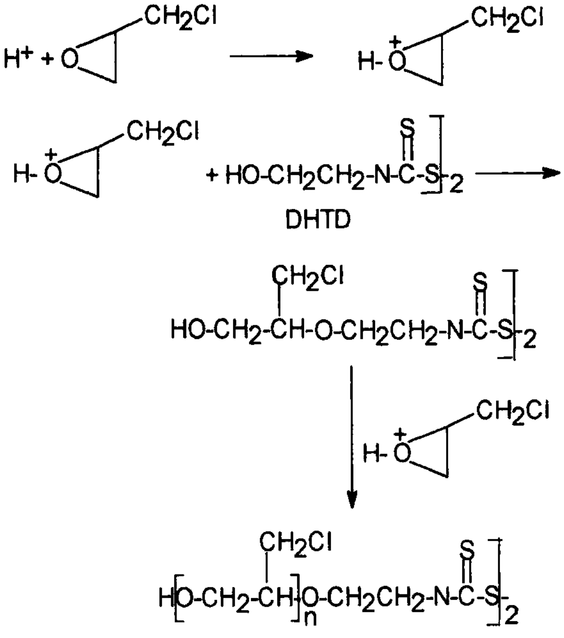
Photo induced radical polymerization of MMA in the presence of PECH having thiuram disulfide group was carried out in bulk at 30 °C for 12 h. Polymerization tubes were irradiated by a 400 w high-pressure mercury lamp at a constant distance of 10 cm.

Characterization of the products:

To confirm the structure of the copolymer obtained, IR and ^{1}H-NMR spectrometry were used. IR spectra were recorded for polymer films cast from benzene solutions in a Schimadzu IR-408 spectrometer. ^{1}H-NMR spectra were taken on Bruker-200 spectrometer in $CDCl_3$.

RESULTS AND DISCUSSION

ECH was polymerized using DHTD as a hydroxyl containing compound by the AM polymerization mechanism. Reaction pathways can be represented thus:



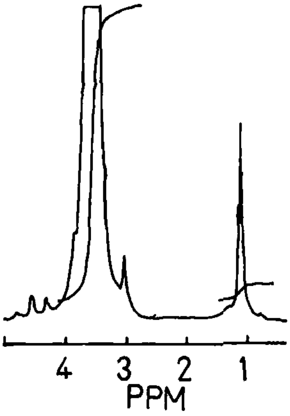
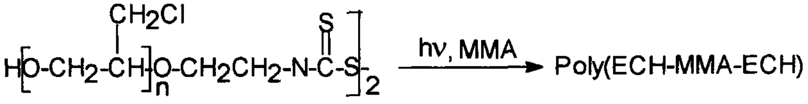


Figure 1. ^1H-NMR spectrum of PECH with thiuram disulfide.

Polymerization was carried out by slow addition ECH to a solution of DHTD and HBF_4 in methylene chloride.

The NMR spectrum in Fig.1 shows the characteristic signals at 3.7-3.2 ppm for the PECH protons, at 3.9 for ppm HO-CH terminal units, at 3.0 ppm for N-CH_2 protons, at 1.1 ppm for $-CH_3$ protons and 1.0 ppm $-CH_2$ protons of PECH possessing thiuram disulfide linkage in the main chain.

PECH having a thiuram disulfide group in the main chain was used in the polymerization of MMA. A solution of PECH (130.5 g/L) in MMA was irradiated for 12 h to obtain ECH-MMA block copolymer with a yield corresponding to 41 % conversion of MMA.



$$\left[H\left[O-CH_2-\overset{\overset{CH_2Cl}{|}}{CH}\right]_n O-CH_2CH_2-N-\overset{\overset{S}{\|}}{C}-S- \right]_2 \xrightarrow{h\nu,\ MMA} \text{Poly(ECH-MMA-ECH)}$$

The NMR spectrum of the ECH-PMMA block copolymer displays signals at 3.8-3.2 ($-CH_2-$, $-CH_2Cl$, -CH- protons of ECH and $-CH_3$ protons of MMA segments), 1.7 ppm ($-CH_2-$ protons of MMA) and 1.1-0.8 ($-CH_3$ protons of MMA).

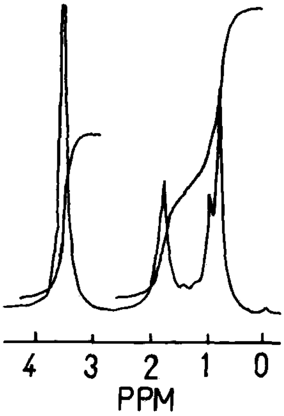


Figure 2. ^{1}H-NMR spectrum of the block copolymer of ECH and MMA

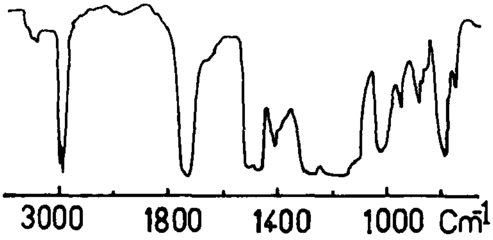


Figure 3. The IR spectrum of the ECH-MMA block copolymer (film)

The IR spectrum of ECH-MMA block copolymer shows characteristic absorptions at 3500 cm-1 (Fig.3) due to -OH group, 1730 cm-1 -C=O, 2900 and 1450 cm-1 -CH2 groups.

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