Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis of Epichlorhydrin-Styrene Block Copolymers via Cation-to-Radical Transformation Process

Ayhan Demirbaş[a]; İsmail Čakmak[a]
[a] Department of Science Education, Karadeniz Technical University, Trabzon, Turkey

To cite this Article Demirbaş, Ayhan and Čakmak, İsmail(1996) 'Synthesis of Epichlorhydrin-Styrene Block Copolymers via Cation-to-Radical Transformation Process', Journal of Macromolecular Science, Part A, 33: 1, 127 — 132
To link to this Article: DOI: 10.1080/10601329608020366
URL: http://dx.doi.org/10.1080/10601329608020366

MACROMOLECULAR REPORTS, A33(SUPPL. 2), 127-132 (1996)

SYNTHESIS OF EPICHLORHYDRIN-STYRENE BLOCK COPOLYMERS VIA CATION-TO-RADICAL TRANSFORMATION PROCESS

Ayhan Demirbaş and İsmail Çakmak
Karadeniz Technical University, Department of Science Education,
Soğütlü-61335 ,Trabzon, Turkey

ABSTRACT

Poly(epichlorhydrin-b-styrene-b-epichlorhydrin) block copolymers were prepared by a two step process via cationic-to-radical transformation in two steps. For this purpose, epichlorhydrin(ECH) was polymerized using HBF_4 as catalyst and reacted with the sodium salt of 4,4'-azo-bis(4-cyanopentanoic acid)(ACPA) to yield PECH possessing thermally labile azo group. PECH-macroazoinitiator was then used to initiate the thermal radical block copolymerization of styrene.

INTRODUCTION

In the synthesis of block copolymers, combination of polymerization types has been used successfully[1]. This route involves transformation reactions in which the mode of propagation of the first monomer is transformed into a different mode suited for the polymerization of the second monomer [2]. One of the these transformations, viz. cation to radical, is essentially based on termination of growing cationic chains with a certain free radical initiators or cationic polymerization of suitable monomers by a functional free radical initiators. The alkali metal salts of some common radical initiators were used as terminating reagent in cationic polymerization of tetrahydrofuran[3-5]. 4,4'-azo-bis-(4-

TABLE 1: Block copolymerization of styrene with PECH Macro-azoinitiator at 70 °C, time: 6hr

Run	PECH (g)	Styrene (g)	Block copolymer Yield(g)	[η], (dL/g)	γ, (ml/ml)
1	0.15	1.00	0.157	0.60	1.80
2	0.35	1.00	0.175	0.40	1.75
3	0.35	1.50	0.306	0.48	1.85
4	0.35	1.67	0.320	0.50	2.08
5	0.35	2.00	0.380	0.50	2.16
6	0.11	2.00	0.190	1.57	2.16
7	0.25	2.00	0.230	0.69	2.00
8	0.50	2.00	0.340	0.67	2.40
9	0.75	2.00	0.500	0.61	2.00
10	1.00	2.00	0.570	0.53	2.08

cyanopentanoyl) chloride, when reacted $SnCl_4$ in the presence of styrene, produces a diacyl cation and polymerization proceeds at two sides by an addition mechanism[6]. The resultant polymers possessing an azo group in the main chain were then used for thermal radical polymerization of a vinyl monomer to obtain block copolymers.

EXPERIMENTAL

Materials:

ECH, styrene, CH_2Cl_2 and HBF_4 were supplied from Merck. ECH purified by fractional distillation and middle fraction was used. Styrene was purified by conventional manner. The disodium salt of ACPA was prepared from ACPA (Fluka) and NaOH according to the reported procedure [3].

Polymerization of ECH:

Into a flask eqipped with a magnetic stirrer, addition funnel and nitrogen bypass were placed 5 ml CH_2Cl_2 and 2 ml of 57 % HBF_4. To this system 20.0 g ECH in 20 ml CH_2Cl_2 was added over 1 h. 2 g of disodium salt of ACPA in 100 ml water was also added and stirred for additional 24 h. After organic phase was dried and evaporated, a viscous liquid obtained(14.5 g 72.5 % yield of ECH).

Block Copolymerization:

Appropriate solutions of PECH having azo group in the main chain and styrene were mixed, degassed and heated at 70 °C for 6 hr in a glass tube. The results are shown in Table 1.

Characterization of the Products:

Fractional precipitation allows the separation of block copolymers from their homopolymers[7]. For this purpose block copolymers were dissolved in THF and aliquot samples of the solutions were taken for the precipitation by adding different volumes of petroleum ether(non-solvent). Homopolymer of polystrene(PS) was separated at different volume ratios of non solvent to solvent(γ = 2.5-3.2 for PS[7])

Viscosity measurements were made with an Ubbelohde viscometer using benzene solutions at 30 °C.

IR spectra was recorded with polymer film, cast from benzene solution, in a Schimadzu IR-408 spectrometer.

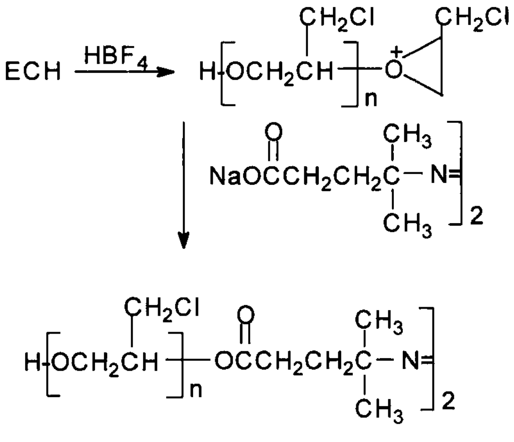
The NMR spectra was obtained from $CDCl_3$ solution on a Bruker 200-MHz NMR spectrometer.

RESULTS AND DISCUSSIONS

PECH with a azo group in the main chain was prepared by a capping reaction between the growing PECH chain and disodium salt of ACPA. Cationic polymerization of ECH was conducted under typical conditions, i.e., by a slow addition of ECH to a solution of HBF_4. Growing PECH chain was terminated by the disodium salt of ACPA to obtain a macro-azoinitiator. Reaction pathways may be represented as follows in Scheme 1.

Thermal decomposition of the azo linkage produces two polymeric radical per chain, which gives rise to block copolymer in the presence of the styrene.

Bulk polymerization of styrene initiated by PECH gave PECH-PS block copolymers. Termination of the polymerization of styrene is mainly by recombination. Therefore, the block copolymer is assumed to have ABA structure.



Scheme 1

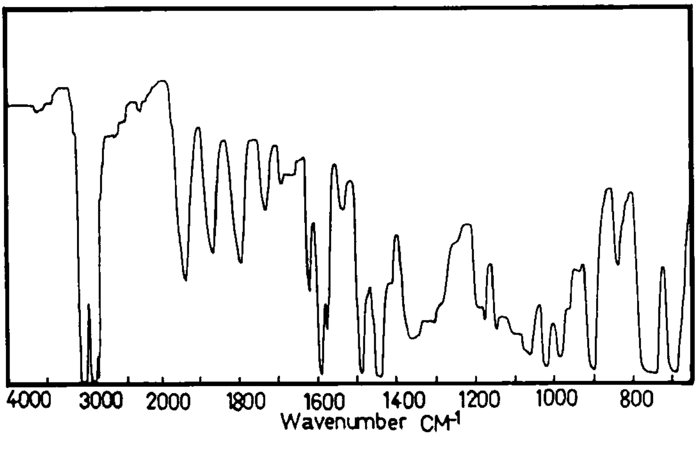


Figure 1. The IR spectrum of the PECH-b-PS-PECH block copolymer(film)

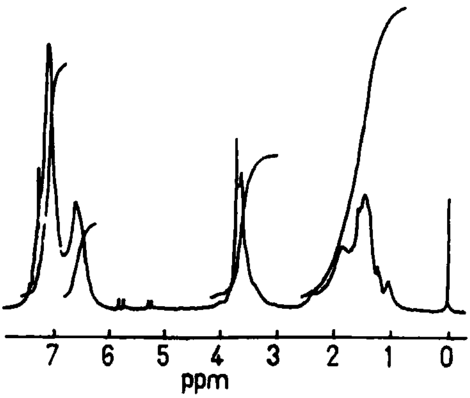


Figure 2. The ^{1}H-NMR spectrum of PECH-b-PS-PECH block copolymer($CDCl_3$)

Characterization of block copolymer films, which are mostly transparent can be summarized as follows:

Fractional precipitation experiments confirmed the block copolymer formation, the γ values of the products are different from their related homo PS in Table 1.

The IR spectrum (Fig. 1) of PECH-PS block copolymer showed characteristic absorptions at 1600 and 700 cm-1 phenyl group of the PS chain.

The ^{1}H-NMR spectrum of PECH-PS block copolymer in Fig.2 shows the characteristic signals at δ (ppm) 6.6-7.2 for phenyl protons of PS chain and 3.6-3.8 -CHI protons of PECH chain.

Acknowledgment

We are indebted to the authorities of the ***KTÜ Araştirma Fonu*** for their financial support.

REFERENCES

1. a) B. Hazer, İ. Çakmak, S. Denizligil and Y. Yağci, *Angew. Makromol. Chem.*, **195**, 121(1992).

b) İ. Çakmak, B. Hazer, Y. Yagci, *Eur. Polym.J.*, **27**, 101(1991).

c) İ. Çakmak, *Macromol. Reports*, **A31(1&2)**, 85 (1994).

2. a)M.J. Stewart, Transformation Reactions, in "New Methods of Polymer Synthesis" (Ed. J.R. Ebdon), Blackie Academic and Professional, Glasgow, UK, 1993 pp.107-137.

   b) Y. Yağci and M. K. Mishra, Block Copolymers via Multi-mode Polymerizations in "Macromolecular Design: Concept and Practice," (Ed. M. K. Mishra), Polymer Frontiers International, Hopewell Jct., NY 1994.
3. F. D'Haese, E.J. Goethals, Y. Tezuka, K. İmai, *Macromol. Chem. Rapid Commun.*, **7**, 165 (1986).
4. F. Burges, Msc. Thesis, University of St. Andrews, 1976.
5. B. Hazer, *Eur. Polym. J.*, **27**, 775 (1991).
6. İ. Çakmak, *Macromol. Reports*, **A31**(2&3), 333 (1994).
7. B. Hazer and B.M. Baysal, *Polymer*, **27**, 96 (1986).