Polymer Bulletin 30, 509–513 (1993)

Polymer Bulletin

Polymerization of carbazolyl-containing epoxides with triphenylcarbenium salts

Pranas Brūzga, Juozas V. Gražulevičius*, Rimtautas Kavaliūnas, Rimantas Kublickas, and Ina Liutvinienė

Department of Organic Technology, Kaunas University of Technology, Radvilėnų Plentas 19, 233028 Kaunas, Lithuania

Summary

Polymerization of 9-(2,3-epoxypropyl)carbazole (EPC) and 1,2-epoxy-6-(9-carbazolyl)-4-oxahexane (ECOH) with triphenylcarbenium hexachloroantimonate and triphenylcarbenium tetrafluoroborate have been studied by the microcalorimetric technique. Triphenylcarbenium salts have turn out to be more efficient catalyst for the polymerization of carbazolyl-containing epoxides than Lewis acids, giving high yields at low initial concentration of the catalyst. Using comparatively restricted conditions of reaction ($[\text{triphenylcarbenium salt}]_0 \geqslant 0.02$ mol/l, $t \geqslant 50^\circ$ C) transition from the conventional active chain end mechanism to the activated monomer mechanism has been observed at a sufficiently high degree of conversion of monomer.

Introduction

Products of ionic polymerization of EPC and ECOH are of interest as organic photoconductors (1,2). The aim of this work was the investigation ofthe polymerization of EPC and ECOH with triphenylmethyl salts: triphenylcarbenium hexachloroantimonate ($Ph_3C^+SbCl_6^-$) and triphenylcarbenium tetrafluoroborate ($Ph_3C^+BF_4^-$). Triphenylcarbenium salts are comparatively stable and effective catalysts which lead to high enough conversions in the cationic polymerization of simple epoxy monomers (3).

Experimental

Materials

EPC (from "Biolar", Latvia) was recrystallized twice from ethyl alcohol (mp 110-111° C). ECOH was synthesized by condensation of 9-(2-oxyethyl)carbazole with epychlorohydrin in the presence of KOH (4). It was purified by recrystallization from ethyl alcohol (mp 57.5-58° C). Triphenyl carbenium salts $Ph_3C^+SbCl_6^-$ and $Ph_3C^+BF_4^-$ (from Aldrich Chemical Co Ltd) were used as obtained. 1,2-dichloroethane (from "Reakhim", USSR) was purified by the conventional procedure (5). Hexane (from "Reakhim") was used as received.

Polymerization

Polymerization was carried out in a 100 ml 3-neck flask, equipped with a mechanical stirrer and a thermometer. The reaction was carried out in 1,2-dichloroethane solution at 30-65°C. The duration of polymerization was of 2.5-15 hours. After polymerization the reaction mixture was carefully washed with distilled water in a separatory funnel and the product of

---

*Corresponding author

polymerization was precipitated in hexane.

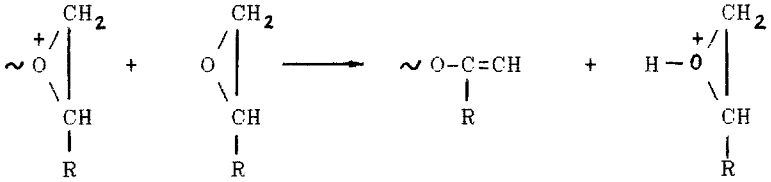
Measurements

Kinetics of EPC and ECOH polymerization were investigated by a microcalorimetry method in isothermal conditions using a differential automatic microcalorimeter DAK 1-1A (from Chernogolovka, USSR) (6). Dynamics of OH-groups in the reaction mixture during polymerization was monitered by the method of IR spectroscopy using spectrometer the "Specord M 80" (from Carl Zeiss Jena). For this purpose the polymerization was carried out in a cell of the sample holder of the spectrometer. Optical density of OH-groups absorption band in the region of 3300-3700 cm^{-1} was recorded periodically.

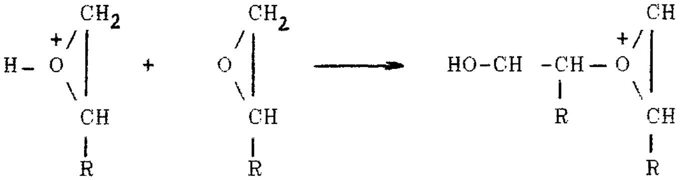
Results and Discussion

The investigation of kinetics of polymerization of the studied monomers with $Ph_3C^+SbCl_6^-$ and $Ph_3C^+BF_4^-$ has revealed that instantaneous initiation is peculiar for these systems, followed by considerable decrease of polymerization rate. However, the decrease of the polymerization rate in these systems is not so dramatic as in the case of the polymerization of the same monomers with Lewis acids (7). The observed higher reactivity of ECOH relative to EPC can be apparently explained by the increase of the distance between the bulky substituent and the epoxy ring.

Analysis of IR-spectra of the oligomers obtained has revealed that they contain hydroxyl end groups as well as $(C_6H_5)_3C$-O- end groups. Hydroxyl end groups apparently appear in the system owing to the chain transfer reaction with participation of monomer by the conventional mechanism of proton transfer from the active centers to the molecules of the monomer:



(1)

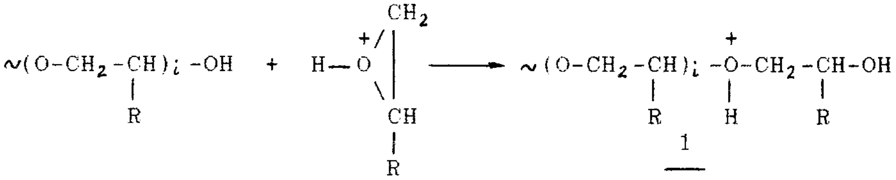


(2)

where R is 2-oxa-4-(9-carbazolyl)butyl or methylene-(9-carbazolyl)

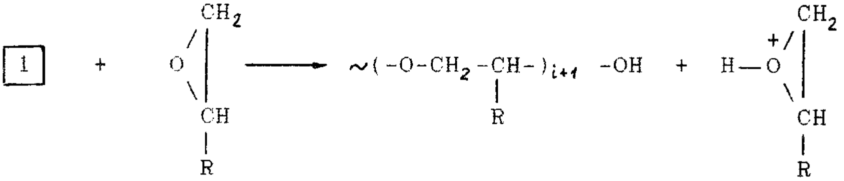
The investigation of polymerization of EPC and ECOH with triphenylmethyl salts by the microcalorimetric technique has revealed that the dynamics of polymerization rate depends on the reaction conditions. At high enough concentrations of catalyst (0.01-0.02 mol/l) and temperatures (above 50°C) i.e. at conditions when the termination reactions are sufficiently intensive, the polymerization rate initially decreases very rapidly, however, after some 0.5-1.5 hrs a spontaneous increase of the polymerization rate is observed (Fig.1).

The similar spontaneous increase of the polymerization rate we have also observed for the polymerization of carbazolyl-containing epoxides with Lewis acids (8). We explain it by the change of the mechanism of polymerization at the higher degrees of conversion of the monomer. When the concentration of OH-groups in the growing chains becomes comparable with the concentration of epoxy monomer, transition from the conventional active chain end mechanism to the activated monomer mechanism takes place. The essence of the activated monomer mechanism lies in the higher nucleofility of ROH relative to that of the epoxy monomer (9). The propogation by this mechanism occures as follows:



$$\sim(\text{O-CH}_2\text{-}\underset{\displaystyle R}{\text{CH}})_i\text{-OH} + \text{H-}\overset{+}{\text{O}}\!\left\langle\begin{matrix}\text{CH}_2\\ \mid\\ \underset{\displaystyle R}{\text{CH}}\end{matrix}\right. \longrightarrow \sim(\text{O-CH}_2\text{-}\underset{\displaystyle R}{\text{CH}})_i\text{-}\underset{\displaystyle H}{\overset{+}{\text{O}}}\text{-CH}_2\text{-}\underset{\displaystyle R}{\text{CH}}\text{-OH} \quad \underset{\displaystyle 1}{}$$

(4)



$$\boxed{1} + \text{O}\!\left\langle\begin{matrix}\text{CH}_2\\ \mid\\ \underset{\displaystyle R}{\text{CH}}\end{matrix}\right. \longrightarrow \sim(\text{-O-CH}_2\text{-}\underset{\displaystyle R}{\text{CH}}\text{-})_{i+1}\text{-OH} + \text{H-}\overset{+}{\text{O}}\!\left\langle\begin{matrix}\text{CH}_2\\ \mid\\ \underset{\displaystyle R}{\text{CH}}\end{matrix}\right.$$

(5)

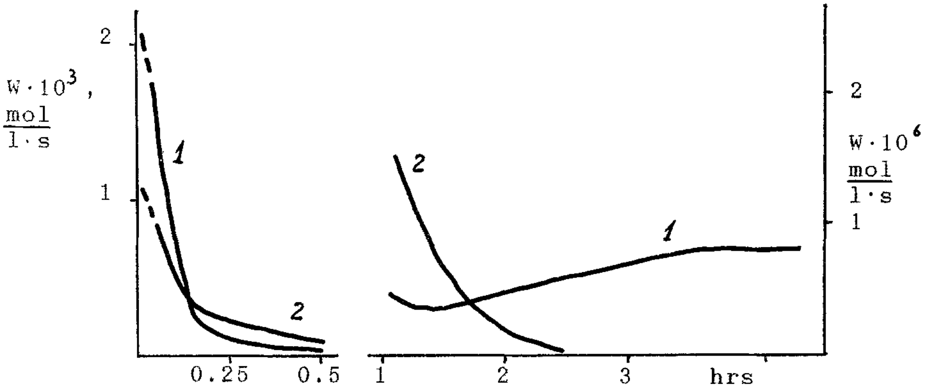


Fig.1. Reaction rate versus time curves for the polymerization of EPC (initial concentration 0.5 mol/l) with $Ph_3C^+SbCl_6^-$.
1 - $[Ph_3C^+ SbCl_6^-]_0 = 0.02$ mol/l; 60°C ;
2 - $[Ph_3C^+SbCl_6^-]_0 = 0.01$ mol/l; 30°C.

At the initial stage of polymerization while the concentration of the monomer strongly exceeds the concentration of OH-groups in the growing chains, activated (protonated) monomer can take part in the propagation by the active chain end mechanism (scheme 2). At low initial concentration of triphenylmethyl salt and at low temperatures no sufficient ammount of protonated monomer and hydroxyl-containing molecules is produced and no change of the reaction mechanism is observed (cf. curve 2 in Fig. 1). Fig. 2 represents the kinetics of the relative concentration change of

OH-groups in the polymerization mixture. For the comparison the kinetic curves of EPC polymerization with $Ph_3C^+BF_4^-$ are also presented in Fig. 2. The similar shape of the curves (monomer conversion) versus time and (relative concentration of OH-groups) versus time is evident. Furthermore, the initial polymerization rate is close to the rate of formation of the OH-groups. However at the final stage of the reaction concentration of OH-groups remains constant while the monomer conversion increases. This observation is characteristic for the polymerization at elevated temperatures (50° C) and at comparatively high initial concentrations of triphenylcarbenium salt ($\geqslant$0.02 mol/l). It is interesting to notice that the end of the increase of the relative concentration of OH-groups (point A on curve 1 in Fig. 2) coincides roughly in time with the onset of the spontaneous increase of polymerization rate discussed earlier. This phenomenon is explanable in terms of polymerization by the activated monomer mechanism. Every act of propagation by this mechanism reproduces the OH-group but does not produce a new one. In the case of the polymerization of EPC or ECOH in mild conditions (temperature <50°C, $[Ph_3C^+ A^-]$ < 0.02 mol/l) the character of the monomer conversion versus time and relative concentration of OH-groups versus time curves remains similar during the whole the process of polymerization. Considerably lower relative concentration of OH-groups in these conditions is also evident from Fig. 2. This observation confirms the above made presumption conserning an insufficient concentration of OH-groups and of the protonated monomer in the system in these conditions to lead to a change of the polymerization mechanism.

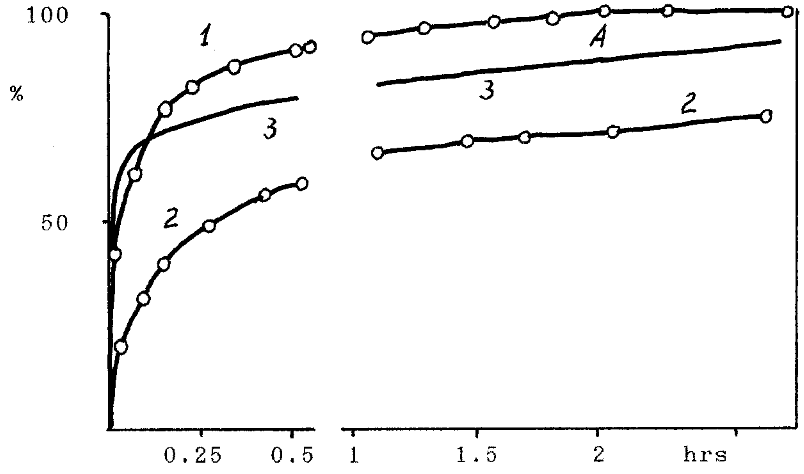


Fig.2. Relative concentration of OH-groups versus time curves (1,2) and conversion versus time curve (3) for polymerization of EPC with $Ph_3C^+BF_4^-$. $[EPC]_0$ =0,4 mol/l. 1,3- 60°C, $[Ph_3 C^+BF_4^-]_0$ =0.02 mol/l, 2- 30°C, $[Ph_3C^+BF_4^-]_0$ =0.01 mol/l.

References

1. Gražulevičius JV, Kavaliūnas R , Undzėnas A, Uss A, Kreivėnienė N (1987) Zh Nauchn Prikl Fotogr Kinematogr 32:26
2. Kavaliūnas R, Undzėnas A, Urbonavičienė J (1982) Zh Nauchn Prikl Fotogr Kinematogr 27:291
3. Vohlidal J, Pacovska M, Dvorak J (1981) Collection Czechoslovak Chem Commun 46: 391
4. Zherebtsov I P, Lipina Z I (1980) Manuscript deposited in ONIITEKhIM. No 949xp-080
5. Weisberger A (ed) (1958) Organic Solvents. Physical Properties and Methods of Purification. Publishing House of the Foreign Litherature. Moscow.
6. Brūzga P, Gražulevičius JV, Kavaliūnas R, Kublickas R (1991) Polym Bull 26: 193
7. Brūzga P, Gražulevičius JV, Kavaliūnas R (1991) Eur Polym J 27: 707
8. Gražulevičius J V, Kublickas R in preparation
9. Penczek S, Kubisa P, Szymanski R (1986) Makromol Chem, Macromol Symp 3: 203

Accepted March 7, 1993 C