Eur. Polym. J. Vol. 27, No. 12, pp. 1411–1416, 1991
Printed in Great Britain. All rights reserved

0014-3057/91 \$3.00 + 0.00

POLYMERIZATION OF CARBAZOLYL-CONTAINING EPOXIDES BY ACTIVATED MONOMER MECHANISM

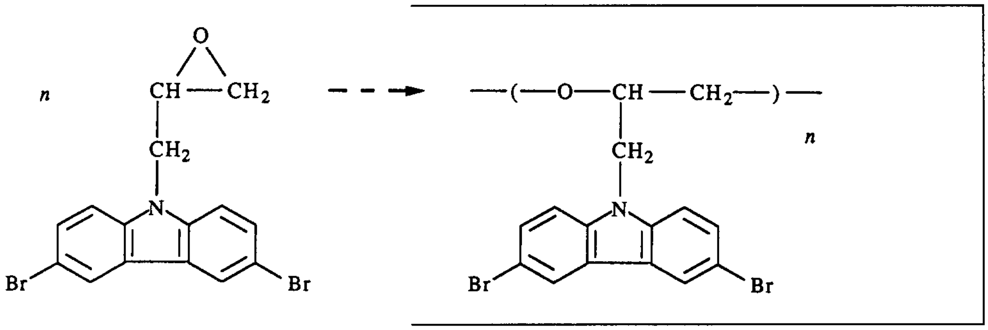
Juozas Vidas Gražulevičius and Rimantas Kublickas
Department of Organic Technology, Kaunas University of Technology, Radvilenu Plentas 19, 233028 Kaunas, Lithuania

(Received 3 April 1991)

Abstract—Cationic polymerization of 3,6-dibromo-9-(2,3-epoxypropyl)carbazole and 9-(2,3-epoxypropyl)carbazole in the presence of hydroxyl-containing compounds has been studied. It has been established that, at a high enough ratio of the concentrations of a hydroxyl-containing compound and monomer, polymerization occurs by an activated monomer mechanism. Linear increase of molecular weight of polymerization products with conversion and hydroxyl functionality of *ca* 2 in the obtained oligomer are characteristic features of activated monomer polymerization observed in this work. Carbazolyl-containing oligomers of comparatively wide range of molecular weight and glass transition temperature were obtained. The low glass transition of the oligomers is explained by the presence of a flexible oxyalkylene fragment into the backbone of the oligomer as well as by the orderly distribution of elementary units in the main chain.

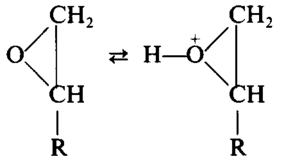
INTRODUCTION

Carbazolyl-containing oligo-ethers and poly[9-(2,3-epoxypropyl)-carbazole] (PEPC) in particular are known as fairly effective organic photoconductors used in electrophotography for the manufacture of microfilms, microfiches and coloured slides [1]. Photoconductivity of electrophotographic materials can be considerably increased by using as photoconductors dibromocarbazolyl-containing oligomers. One such oligomer is poly[3,6-dibromo-9-(2,3-epoxypropyl)carbozole] (PDBEPC) obtained by cationic polymerization of the corresponding epoxy monomer 3,6-dibromo-9-(2,3-epoxypropyl)carbazole (DBEPC):

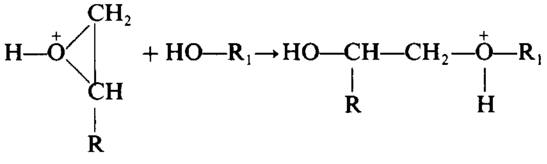


Application of PDBEPC is limited because of its poor mechanical properties resulting from the stiffness of its molecules. The glass transition temperature of cationically obtained PDBEPC is 100–130° [2]. Polymerization of epoxy monomers by an activated monomer (AM) mechanism, described by Polish authors [3–5], seems to offer possibilities of improving mechanical and film-forming properties of PDBEPC and of other oligomers of this kind. The AM mechanism allows introduction of a flexible oxyalkylene fragment into the resulting oligomeric chain, regulation of their molecular weight and elimination of microcyclic byproducts, giving telechelic oligomeric polyethers.

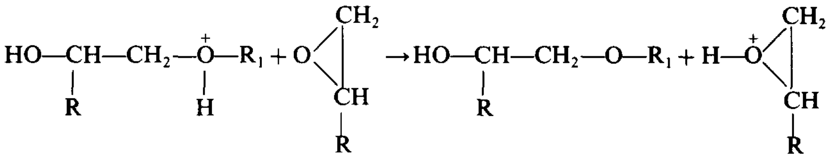
Polymerization by an AM mechanism proceeds when the monomer is in equilibrium with its activated form:



If the instantaneous concentration of the monomer does not exceed that of hydroxyl groups in the system, propagation proceeds by addition of a protonated monomer molecule to the HO-terminated, electrically uncharged growing macromolecule [3]:



Simultaneously, transfer of proton to another molecule of the monomer (regeneration of AM) occurs:



The tendency of AM to interact with a hydroxyl-containing molecule but not with the epoxy monomer results from the lower nucleophility of the latter.

EXPERIMENTAL PROCEDURES

DBEPC was synthesized by bromination of 9-(2,3-epoxypropyl)-carbazole (ECP) with *N*-bromosuccinimide as described [5]. It was purified by recrystallization from toluene. m.p. 141–142°. EPC ("Biolar", Latvia) was recrystallized from ethanol. m.p. 110–111°. $BF_3{\cdot}O(C_2H_5)_2$ was refluxed over CaH_2 and distilled. b.p. 126–127°. 1,2-Ethanediol and 1,4-butanediol ("Reakhim", U.S.S.R.) were distilled *in vacuo*. 1,3-Propanediol (from Merck) was used as received. 9-(2-Oxypropyl) carbazole (OPC) was synthesized and purified as described [6]. 1,2-Dichloroethane was refluxed over P_2O_5 and distilled. Hexane was used as received.

Polymerization of DBEPC and EPC in the presence of hydroxyl-containing compounds was carried out in a flask, equipped with a mechanical stirrer and a thermometer. Reaction was carried out in 1,2-dichloroethane solution at 45° under N_2. $BF_3{\cdot}O(C_2H_5)_2$ was used as catalyst; its initial concentration ranged from 0.05 to 0.2 mol/l. The initial concentration of hydroxyl-containing compound was 0.05–0.4 mol/l. The initial concentration of DBEPC was 0.3–0.5 mol/l and that of EPC 0.4–0.6 mol/l. Two methods were used for introduction of monomers into the system. Either the whole of the monomer was added to the initial reaction mixture before introduction of the initiator or its solution was added in small portions during polymerization (30–60 min). The reaction was monitored by taking small samples which were then diluted with *N,N*-dimethylformamide to stop polymerization and to prepare them for GPC analysis. The duration of polymerization was 2–3 hr. On completion of the reaction, residual catalyst was neutralized with a twofold excess of 25% ammonium hydroxide. Then the reaction mixture was carefully washed with distilled water and the product of polymerization was precipitated in hexane. The resulting oligomer was filtered off and dried *in vacuo* at ambient temperature. The yield of oligomers was 70–75%.

Number-average molecular weights of the oligomers were determined by vapour pressure osmometry using Knauer apparatus with toluene as solvent.

Conversion of DBEPC and EPC and molecular weight distribution of oligomers were estimated by GPC ("Sephadex LH-20" gel, *N,N*-dimethylformamide eluent). Consumption of 1,3-propanediol was monitored by gas chromatography (Chrom-5, Czechoslovakia). Microcalorimetry was used for the estimation of polymerization rate (differential microcalorimeter DAK 1-1A, Chernogolovka, U.S.S.R.). Details of the procedure have been described [7]. The composition of the products of polymerization was determined by u.v. spectroscopy and by elemental analysis. Hydroxyl-number was found by a standard procedure [8].

RESULTS AND DISCUSSION

Cationic polymerization of DBEPC by an AM mechanism was studied using $BF_3{\cdot}O(C_2H_5)_2$ as a catalyst and 1,2-ethanediol, 1,3-propanediol or 1,4-butanediol as proton-donor. Depending on the ratio of the initial concentrations of the monomer and glycol, oligomers of a rather wide range of molecular weights ($\bar{M}_n$ from 800 to 1480) and glass transition temperature (T_g from 26 to 85°) were obtained. It has been established that, on average, one fragment of glycol enters every molecule of the product of polymerization. Therefore, because of the comparatively low degree of polymerization of the synthesized oligomers, they will be called co-oligomers of DBEPC and glycols. For a wide range of initial concentrations of glycol and monomer, hydroxyl functionality of the synthesized co-oligomers was found to be *ca* 2, showing that no cyclics are produced in these systems.

Traditional active chain-end cationic polymerization of DBEPC with $BF_3{\cdot}O(C_2H_5)_2$ usually leads to oligomers of $\bar{M}_n$ *ca* 1100–1300. Molecular weight in this case is almost independent on the conditions of polymerization. In the presence of glycols, co-oligomers of these and even slightly higher molecular weight can be synthesized only at high ratios of the initial concentrations of glycol and monomer (2:1 to 1:1) when portions of DBEPC solutions are gradually introduced into the reaction mixture. T_g of these co-oligomers is rather high (75–85°) but it is considerably lower than that of PDBEPC obtained by cationic polymerization of the corresponding monomer without using glycols (by the active chain-end mechanism). T_g of cationically obtained PDBEPC of $\bar{M}_n$ 1100–1300 is 100–115°. Thus low T_g of the co-oligomers obtained by cationic polymerization of DBEPC in the presence of glycols (via an AM mechanism) is determined not only by their low molecular weight but also by peculiarities of the backbone of the molecules (presence of fragments of glycol and distribution of DBEPC elementary units). The low molecular weight as well as the structure of the main chain lead also to good film-forming properties of co-oligomers of DBEPC and glycols.

If the ratio of the initial concentrations of glycol and the monomer was high enough (0.8–0.4), the investigated systems showed features of a living polymerization. Addition into the reaction mixture of fresh monomer led to increase of yield and molecular weight of the co-oligomers.

At a favourable ratio of glycol, DBEPC and catalyst, another peculiarity of AM polymerization was observed. It is evident from the data presented in Fig. 1 that $\bar{M}_n$ linearly increases with conversion of DBEPC when the ratio of $[1,3\text{-propanediol}]_0/[DBEPC]_0$ is high enough. This phenomenon as well as the hydroxyl functionality of two for the resulting polymers are the main characteristics of cationic polymerization of epoxy monomers by an AM mechanism [2, 9].

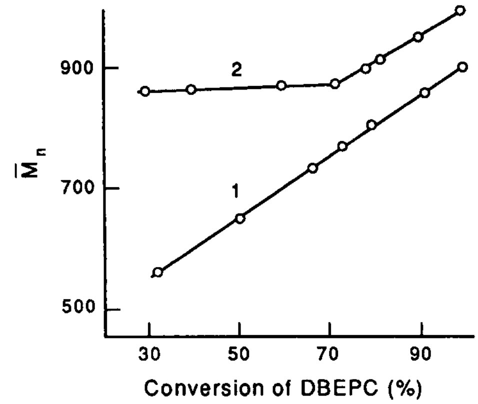
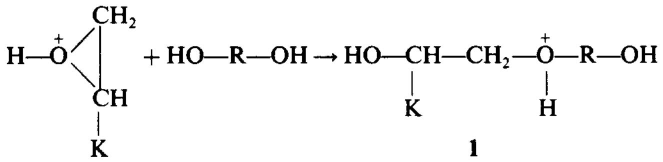


Fig. 1. Relationship between conversion of DBEPC and $\bar{M}_n$ of co-oligomer. 1, 30°; $[DBEPC]_0 = 0.4$ mol/l; $[BF_3{\cdot}O(C_2H_5)_2]_0 = 0.08$ mol/l; $[1,3\text{-propanediol}]_0 = 0.20$ mol/l; 2, 60°; $[DBEPC]_0 = 0.3$ mol/l; $[BF_3{\cdot}O(C_2H_5)_2]_0 = 0.05$ mol/l; $[1,3\text{-propanediol}]_0 = 0.05$ mol/l.

The mechanism of formation of co-oligomers of DBEPC and glycols under the action of $BF_3{\cdot}O(C_2H_5)_2$ could be envisaged as follows. It is known [10] that BF_3 easily forms complexes with electron-donating compounds. Since basicity of the epoxy monomer is lower than that of the glycol, apparently BF_3 forms complex with glycol but not with the monomer:

$$BF_3{\cdot}O(C_2H_5)_2 + HOROH \rightarrow H^+BF_3^-OROH + (C_2H_5)_2O. \quad (1)$$

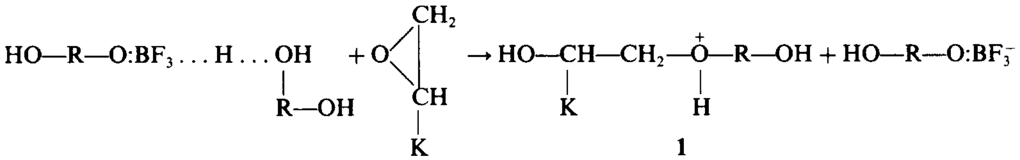
The lack of the violet-brownish colour of the reaction mixture which is characteristic of DBEPC polymerization with $BF_3{\cdot}O(C_2H_5)_2$ (and donor–acceptor complexes of BF_3 with carbazolyl-containing compounds generally [11]) could be indirect evidence of utilization of BF_3 for the formation of the complex with glycol. The complex $H^+BF_3^-OROH$ apparently protonates the monomer which further interacts preferably with diol as the more basic compound:



(2)

where K is methylen-[9-(3,6-dibromocarbazolyl)].

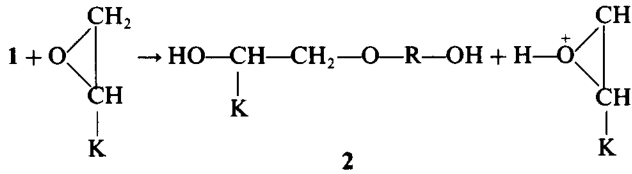
Compound **1** can result also from the interaction of DBEPC with the double complex of BF_3 [10]:



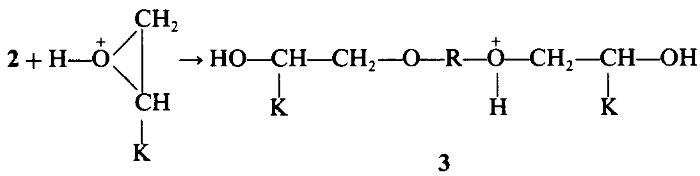
(3)

Thus in this reaction, the diol acts as an initiator and is consumed in the early stages of the process. This idea is confirmed by the data of Fig. 2 which shows conversion vs time for 1,3-propanediol and for DBEPC.

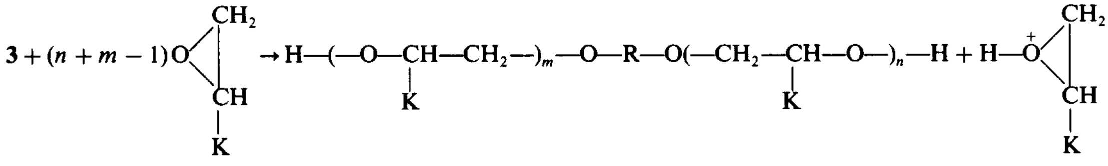
The interaction of initiating species **1** with the monomer leads to formation of AM which can react with another molecule of diol and (after consumption of diol) to chain growth by the AM mechanism:



(4)



(5)



(6)

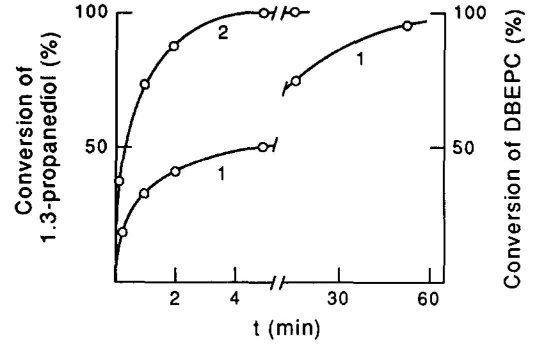
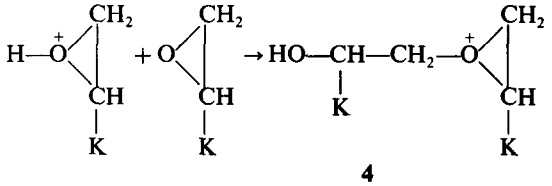


Fig. 2. Conversion vs time for DBEPC (1) and 1,3-propanediol (2) at 40°. $[DBEPC]_0 = 0.4$ mol/l; $[1,3\text{-propanediol}]_0 = 0.2$ mol/l; $[BF_3{\cdot}O(C_2H_5)_2]_0 = 0.05$ mol/l.

Investigation of the changes of molecular weight distribution during cationic polymerization of DBEPC in the presence of diols by the AM mechanism has revealed that, at the beginning of polymerization while there is sufficient starting diol in the system, the proportion of higher oligomers (of DP 2 and higher) is very small (Fig. 2, curve 1). The largest proportion is of the low-molecular compound **2** (maximum at elution volume *ca* 49 ml). When the starting diol is consumed, the increase of the monomer leads to decrease of the proportion of compound **2** in the reaction mixture (*cf* curves 2 and 3 Fig. 2). This observation indicates that propagation mainly involves compound **2**.

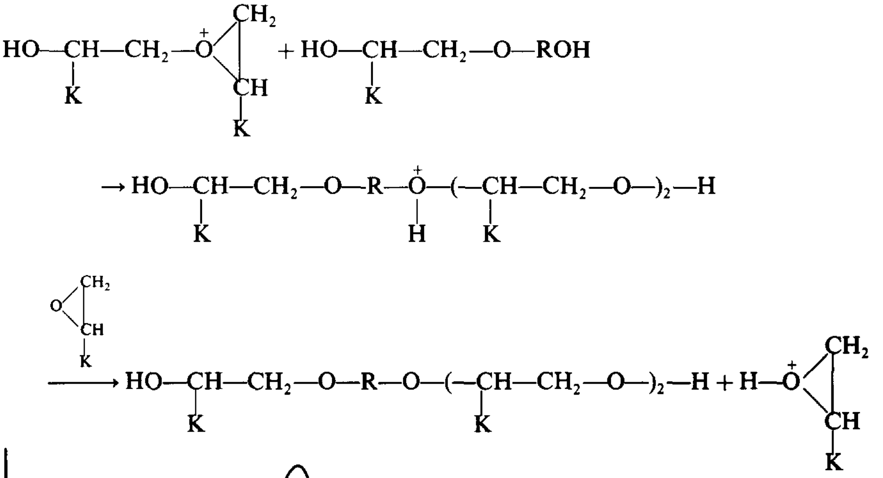
If the ratio DBEPC:diol (starting diol plus macrodiol) in the system is too high, deviation from AM is possible and some DBEPC molecules participate in propagation by a conventional active chain-end mechanism:



4

(7)

Such active species can take part in chain transfer to the monomer and the reaction mixture may contain some macromolecules of unit hydroxyl functionality. However when surplus monomer is consumed, return to the AM mechanism is possible [2, 4]:



(8)

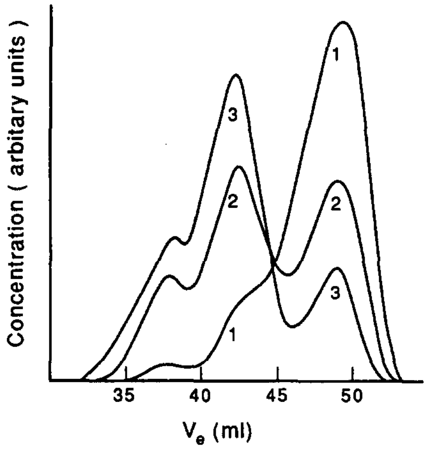


Fig. 3. Elution curves for reaction mixtures of DBEPC polymerization at 30° in the presence of 1,3-propanediol at various degrees of DBEPC conversion: 1, 34%; 2, 72%; 3, 100%; $[DBEPC]_0 = 0.4$ mol/l; $[BF_3{\cdot}O(C_2H_5)_2]_0 = 0.08$ mol/l; $[1,3\text{-propanediol}]_0 = 0.20$ mol/l. Peak for the monomer is eliminated.

The fact that, at high ratios of the initial concentrations of DBEPC and diol, the products of polymerization possess hydroxyl functionality of *ca* 2 indicates that reaction (8) is more significant during termination of propagation by the active chain-end mechanism than chain transfer to monomer (7).

Microcalorimetric investigation of cationic DBEPC polymerization in the presence of diols has revealed that, at the initial concentration of diol sufficient to induce polymerization by the AM mechanism, polymerization is faster than the analogous reaction under the same conditions but without diols (Fig. 3). At low concentration of the starting diol, the initial polymerization is slower but, after a certain time (1–2 hr), spontaneous increase of polymerization rate is observed (after a significant fall) which could indicate "returning" to the AM mechanism. Data on the alteration of molecular weight (*cf* Fig. 1, curve 2) confirm this view. Similar change from the prevailing active chain-end mechanism to the AM mechanism has already been discussed [12].

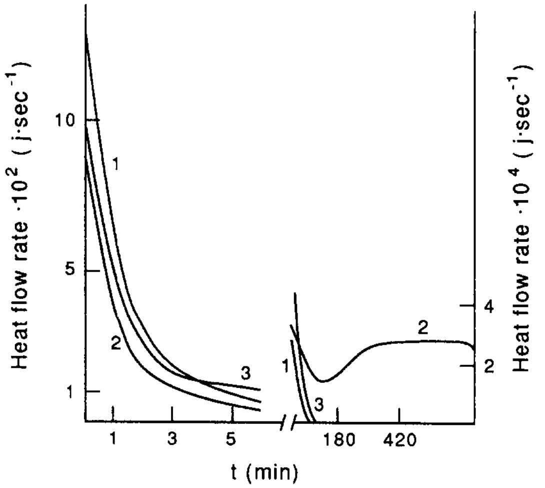


Fig. 4. (Heat flow rate) vs time for DBEPC polymerization with $BF_3 \cdot O(C_2H_5)_2$ at 60°. $[DBEPC]_0 = 0.3$ mol/l; $[BF_3 \cdot O(C_2H_5)_2]_0 = 0.05$ mol/l. Initial concentration of 1,3-propanediol: 1, 0.20 mol/l; 2, 0.05 mol/l; 3, 0.00 mol/l.

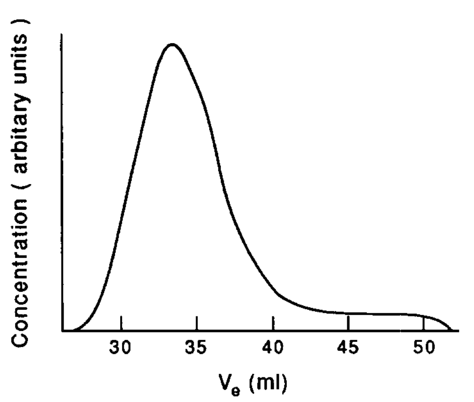


Fig. 5. Elution curve for product of polymerization of DBEPC in the presence of poly(ethylene glycol)-600. Conditions of polymerization: [DBEPC] = 0.4 mol/l (gradual introduction of DBEPC solution into the reaction mixture); $[BF_3 \cdot O(C_2H_5)_2]_0 = 0.1$ mol/l; 60°; [poly(ethylene glycol)-600]$_0$ = 0.3 mol/l.

Using AM polymerization, block copolymers of DBEPC and poly(ethylene glycol) have been synthesized. Figure 4 shows the elution curve of block copolymer of DBEPC and poly(ethylene glycol)-600. A very low concentration of a low molecular fraction containing no poly(ethylene glycol) in this product indicates that homopolymerization of DBEPC in the system is almost suppressed. Synthetic possibilities of AM polymerization have also been studied using another carbazolyl-containing epoxy monomer viz. EPC. Table 1 presents some characteristics of co-oligomers of EPC (DBEPC) and diols. For comparison, analogous characteristics are shown for oligomers synthesized without using diols i.e. by active chain-end polymerization. Considerably lower T_g of co-oligomers of EPC and diol than of oligomer (of similar molecular weight) synthesized by EPC polymerization with $BF_3 \cdot O(C_2H_5)_2$ is evident. The decrease of T_g of the resulting oligomers found on changing from active chain-end polymerization to AM polymerization is higher for EPC oligomers than for DBEPC oligomers. Apparently low T_g of the co-oligomers of EPC with diols results not only from introduction of a flexible diol residue into the main chain of the oligomer but also by the distribution of elementary units in the backbone.

In the excellent work [4] of Penczek, it was established that, for AM polymerization of substituted epoxides, both the primary and secondary hydroxyl groups react predominantly with the least substituted carbon atom of the epoxy ring. As a result, the oligomer of epichlorohydrin is composed almost exclusively of head-to-tail repeating units. Since the steric influence of a substituent predominantly determines this regularity [4], it is very likely that head-to-tail repeating units predominate also in the products of polymerization by the AM mechanism of carbazolyl-containing epoxides. In conventional cationic polymerization, usually both α-(opening of O—CH—R bond) and β-ring opening (scission of O—CH_2 bond) occurs [13]. Considerably lower T_g of EPC oligomers obtained weight synthesized by active chain-end cationic polymerization, is apparently caused by the regular distribution of elementary units in the backbone. To support this idea, AM polymerization of EPC was carried out using a monohydroxylic carbazolyl-containing compound 9-(2-oxypropyl)carbazole as source of protons; this compound leads to increased flexibility of molecules of the resulting oligomer. It is evident from Table 1 that T_g of this oligomer is 15° lower than that of PEPC obtained by conventional cationic polymerization. For DBEPC, such a phenomenon was not observed. Apparently a steric effect due to heavy Br atoms influences the conventional cationic polymerization in such a way that it leads to oligomers in which head-to-tail units prevail.

Table 1. Conditions of synthesis and characteristics of the oligomers and co-oligomers of EPC and DBEPC

Starting hydroxyl-containing compound	Monomer	Initial ratio $\frac{[\text{monomer}]_0}{[\text{diol}]_0}$	Total ratio $\frac{[\text{monomer}]}{[\text{diol}]}$	$\bar{M}_n$	$\frac{\bar{M}_w}{\bar{M}_n}$	T_g	Hydroxyl functionality
—	EPC	—	—	1000	1.20	93	0.70
1,3-Propanediol	EPC	0.5	4.5	1060	1.12	45	2.00
1,2-Ethanediol	EPC	3.0	3.0	720	1.13	33	1.99
OPC	EPC	0.5	4.0	1040	1.13	78	0.99
—	DBEPC	—	—	1250	1.20	102	0.82
1,3-Propanediol	DBEPC	0.5	3.3	1280	1.12	80	2.00
1,2-Ethanediol	DBEPC	3.0	3.0	1100	1.13	75	1.99

Acknowledgments—The authors thank Dr P. Kubisa (Center of Molecular and Macromolecular Studies, Łódź, Poland) who generously shared his expertise, Professor S. Kutkevičius and Dr I. Nemanienė (both from Kaunas University of Technology) for supplying DBEPC and 9-(2-oxypropyl)carbazole. The authors are also grateful to Professor R. Venskutonis (Kaunas University of Technology) for help in monitoring diol consumption by gas chromatography.

REFERENCES

1. I. Vapšinskaitė, J. Rakauskas and A. Girdžiušas. *Zh. Nauchn. Prikl. Fotogr. Kinematogr.* **27**, 255 (1982).
2. S. Penczek, P. Kubisa and R. Szymanski. *Makromolek. Chem., Macromolec. Symp.* **3**, 203 (1986)
3. P. Kubisa. *Makromolek. Chem., Macromolec. Symp.* **13/14**, 203 (1988).
4. T. Biedron, R. Szymanski, P. Kubisa and S. Penczek. *Makromolek. Chem., Macromolec. Symp.* **32**, 155 (1990).
5. A. Stanišauskaitė and A. Leitaitė. Manuscript deposited in LIMTI No. 1403 (1985).
6. *Ger. Pat.* 1 173 797 (1964); invs.: M. Paul and T. Cassier.
7. P. Brūzga, J. V. Gražulevičius, R. Kavaliūnas and R. Kublickas. *Polym. Bull.* (in press).
8. A. Verley and F. Bolsing. *Berichls* **34**, 3354 (1901).
9. Y. Okamoto. Cationic ring-opening polymerization of epichlorohydrin in the presence of ethylene glycol. In *Ring Opening Polymerization. ACS Symposium Series* **187**, 361 (1985).
10. A. M. Eastham. Epoxy compounds. In *The Chemistry of Cationic Polymerization* (edited by P. H. Plesh). Mir, Moscow (1966).
11. *USSR Pat.* 1027684 (1983); inv. A. Undzėnas.
12. J. V. Gražulevičius, R. Kublickas, R. Kavaliūnas and P. Kubisa. *Makromolek. Chem.* (in press)
13. Z. J. Jedlinski, M. Bero, J. Kasperczyk and M. Kowalczuk. Polymerization of substituted oxiranes, epoxy aldehids, and derived oxacyclic monomers. In *Ring Opening Polymerization. ACS Symposium Series* **187**, 205.