Highly Branched (Starlike) Polymers Obtained by Reacting Oligoalcohols with Dicyclic Compounds. 1. Monomethoxy Poly(ethylene oxide) and Diepoxides

Grzegorz Lapienis and Stanislaw Penczek*

Center of Molecular and Macromolecular Studies,
Polish Academy of Sciences, 90-363 Lodz,
Sienkiewicza 112, Poland

Received January 24, 2000

Revised Manuscript Received June 26, 2000

The present paper follows our patent application[1] filed in 1998 and previous presentations at polymer symposia.[2,3]

"Arms-first" and "core-first" star polymers have mostly been developed for vinyl polymers. This field, opened by Rempp and his colleagues[4] in 1968 for anionic polystyrene (PS)−divinylbenzene (DVB), was a subject of numerous further developments, summarized recently in Rempp's review papers.[5,6] Cationic vinyl polymerizations, giving polyisobutylene[7] or poly(vinyl ether)[8] starlike polymers were also recently developed by a similar approach. Starlike poly(ethylene oxides) (PEO) were anionically prepared by Lutz et al. with a polyDVB core.[9] Some related approaches were described by Gnanou[10] and the most recently by Frechet,[11] who prepared highly branched polyethers with epoxy end groups. Highly branched polyethers−polyols were also prepared by cationic[12] and anionic polymerization of glycidol.[13]

Our work is related to Rempp's approach for styrene/DVB.[4] In our present work oligomeric alcohols are converted into the alkoxide anions and reacted with diepoxy compounds. The resulting reactive starlike macromolecules contain multialkoxide anion cores and can either be functionalized at this stage or initiate polymerization of another monomer. The method described in the present note allows preparation of branched polymers with homo- or heterobranches and with end groups that are at will prepared from the alkoxide anions.

Results and Discussion. Reactions of alkoxide anions with substituted oxiranes are well-known.[14] Nucleophilic substitution proceeds mostly at the least substituted carbon atom, with ring-opening and formation of the substituted (e.g., secondary) alkoxide anion.

In the present note we describe the highly branched structures prepared from monomethoxy poly(ethylene oxide) alkoxide anion and diepoxides. The kinetics of their formation studied by MALDI−TOF−MS is described elsewhere;[15] in this communication, we merely give evidence for the multibranched star formation. Other macromolecular alcohols as precursors of the first arms will also be described elsewhere.[15]

The overall scheme of the star polymer formation by the method described in this paper is shown in Scheme 1.

All of these stages were performed with a living poly(ethylene oxide) anion with various diepoxides; mostly the diglycidyl ether of ethylene (DGEEG) or neopentyl glycol (DGENPG).

Thus, if an alcohol/alkoxide anion mixture reacts with the diepoxide (DE) there is a sequence of parallel−consecutive reactions that could lead to the network formation at a certain conversion of epoxy groups (cf. Scheme 1). A large number of longer chains attached to such a core keep macromolecules in solution. In Table 1 the gel formation as a function of the first arms length and arm/diepoxide ratio is given (bulk, 80 °C).

The consecutive stages of product formation were slow enough to be followed by ^{1}H NMR, as described in the next paragraphs. Moreover, application of the MALDI−TOF−MS allowed step by step observation of the process of hyperbranching.[15]

I. Observation of Stages 1, 2, and 3 by ^{1}H NMR. Conversion of the original primary into the mostly secondary (second stage) and back to primary −OH groups (third stage).

1. Stage 1. Formation of the First Arms. This does not require a detailed description. EO was polymerized with *t*-BuOCs in THF as solvent. The calculated M_n of the precursors agree with M_n (average) determined by three different analytical methods (^{1}H NMR from two end groups, SEC and MALDI−TOF−MS[15]). In three experiments for calculated M_n of precursors—3050, 2290, and 2340—the corresponding respective values of determined M_n (average) were observed: 2930, 2330, and 2150.

In the ^{1}H NMR spectra of the precursor macromolecules, capped with trifluoroacetic anhydride, exclusively esters of primary alcohols, $-CH_2OC(O)CF_3$ ($\delta = 4.5$ ppm), are observed (Figure 1A). The electronic integrations of the tail ($-CH_2OC(O)CF_3$)) and head ($(CH_3)_3C-$) end groups agree well (close to 1:4.5).

2. Stage 2. Formation of the Core with Attached Arms. Reaction of diepoxides with the precursor arms should predominantly give secondary alkoxide anions from the primary ones present in precursor. Any next reaction of diepoxide with the first generation of the secondary alkoxide anions formed in this way should reproduce mostly secondary alkoxide anions in consecutive generations.

The ^{1}H NMR spectrum of the product of the second stage killed with AcOH and then reacted with $(CF_3CO)_2O$ is shown in Figure 1B.The absorption at $\delta = 4.5$ ppm (esters of primary alcohols $-CH_2OC(O)CF_3$) is converted into $\delta = 5.3$ ppm (esters of secondary alcohols: $>CHOC(O)CF_3$). Integration of $-CH-$ and $(CH_3)_3C-$ give a ratio of approximately 1:6 in place of 1:9. A tentative explanation is given below, in the next section.

3. Stage 3. Polymerization from the Reactive Core. The product of the second stage was used as an initiator for further polymerization of ethylene oxide. When polymerization was completed, the alkoxide anions were finally killed with $(CF_3CO)_2O$; absorption at $\delta = 5.3$ ppm (cf. Figure 1B) disappears and absorption reappears at $\delta = 4.5$ ppm (Figure 1C), indicating reconversion of the secondary back to primary −OH groups. Integration of $CH_2/(CH_3)_3$ is identical to the product of the second stage; i.e., 1:3 (corresponding to 1:6 in the second stage) in place of 1:4.5. This indicates that conversion of the secondary alkoxide anions in core to the primary alkoxide anions in the new generation of arms is close to quantitative. Thus, formation of a

10.1021/ma000115n CCC: $19.00

Scheme 1

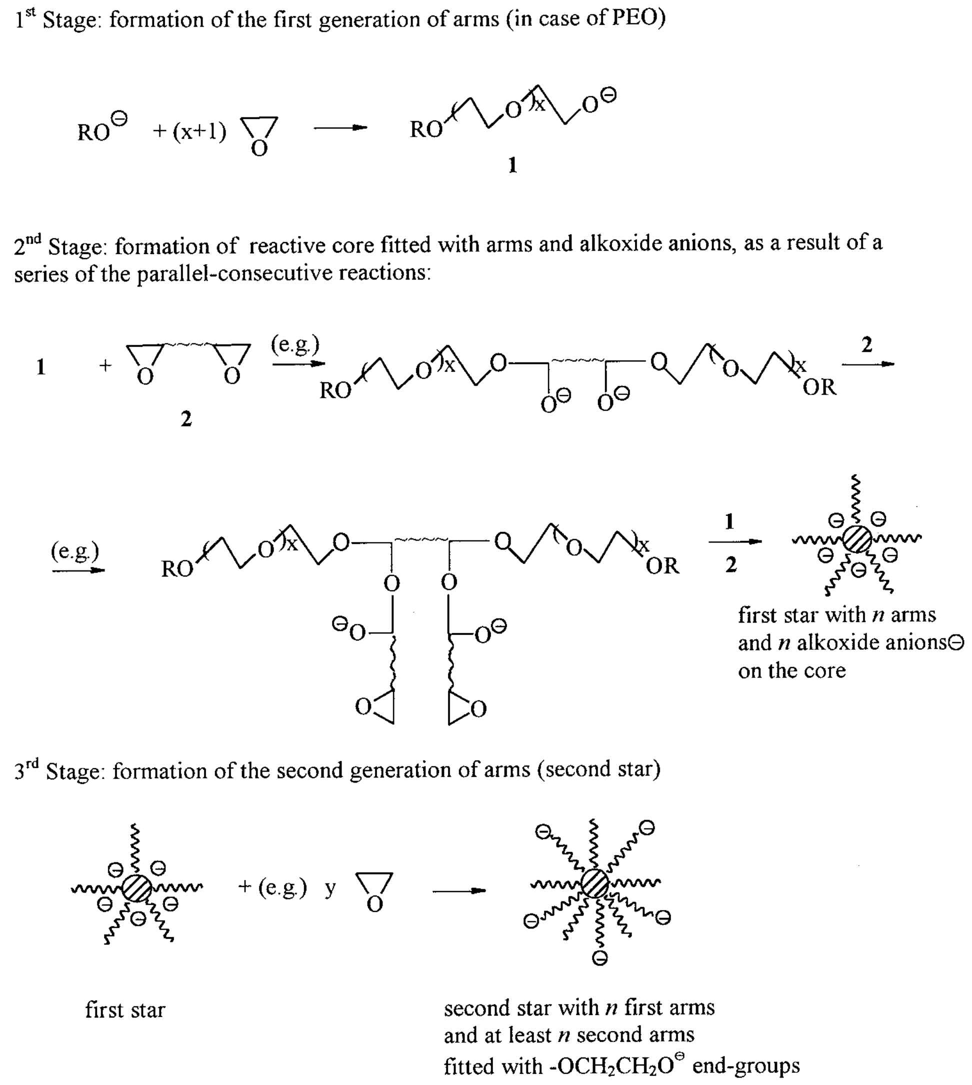

Table 1. Branching of Monomethoxy Poly(ethylene glycol) (MPEG) with Diglycidyl Ether of Neopentyl Glycol (DGENPG) at 80 °C in Bulk[a]

	ratio: DGENPG/MPEG					
M_n of MPEG	0.60	0.78	1.28	1.60	1.92	3.84
296	soluble (106 h)	gel (6.5 h)				
550			soluble (12.5 h)	gel (32 h)		
2000					soluble (69 h)	gel (9.5 h)

[a] In parentheses is given the reaction time; soluble at complete conversion of epoxy groups (according to ^{1}H NMR).

larger number of the −OH groups than introduced originally with the precursor took place at the second stage presumably resulting from a proton transfer.

II. High Molar Mass Branched Macromolecules and Their Analysis. Two examples of the high molar mass branched macromolecules formation are given below. Thus, *t*-BuOCs initiated polymerization of EO was used to prepare arms: $M_n = 2230$ (^{1}H NMR end groups analysis) (2340 (calculated)). Then these oligomeric alkoxides were reacted with DGEEG, taking the DGEEG/first arms ratio equal to 2.13. In the third stage EO was polymerized to complete conversion giving second generation of arms. The calculated M_n of the second arms is 10870 assuming their "identity". The resulting branched macromolecules were terminated with $POCl_3$ (large excess) and converted into $-OP(O)(ONa)_2$ end groups. All reactions were conducted in a "one pot" manner. The molar mass of this final product was determined by membrane osmometry ($M_n = 51\,100$), SEC ($M_n = 52\,700$; $M_w = 116\,000$), MALLS ($M_w = 114\,000$ (from Zimm plot). Both SEC and MALLS were measured in H_2O with addition of 0.1% NaN_3. The number of arms is close to 17, provided that all of the above made assumptions are correct. In the $^{31}P\{^1H\}$ NMR spectrum only one signal at $\delta = 4.73$ ppm was observed; thus, exclusively monoesters of H_3PO_4 are present.

The other fraction of the mentioned above polymer was terminated with water giving macromolecules with −OH end groups ($M_n = 131\,500$; membrane osmometry). Calculated number of arms: 20. The intrinsic viscosity for this polymer (with −OH end groups) was measured in 0.1% NaCl at 25 °C giving $[\eta]$ equal to 15.5.

According to Roovers[16] star-shaped poly(ethylene oxide)s with 16 arms and $M_w = 130\,000$ have $[\eta]$ equal to 29.5 mL/g. If we roughly extrapolate his data to a

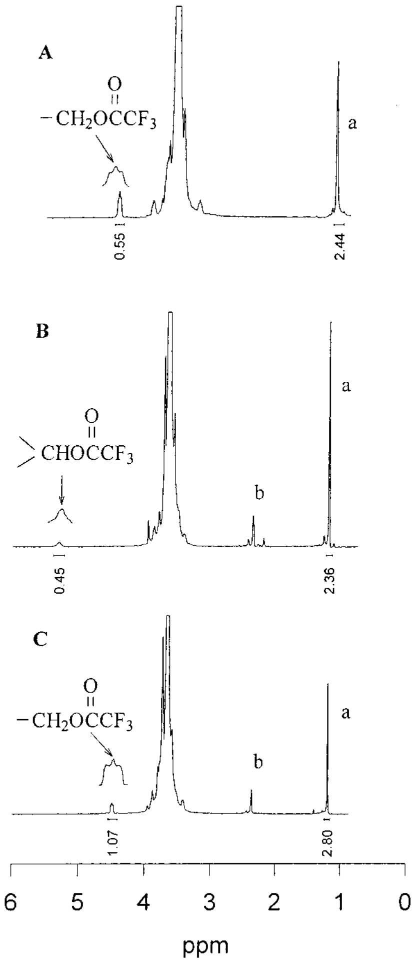

Figure 1. Determination of the structure of products by ^{1}H NMR spectra (in $CDCl_3$ with addition an excess of $(CF_3CO)_2O$). Below the signals of end groups, electronic integrations are given: (a) *t*-BuO end group; (b) residual CH_3COOH. Key: (A) first stage, formation of the first generation of arms (primary alkoxide anions); initiation, *t*-BuOCs; (B) second stage, formation of the core (secondary alkoxide anions); (C) third stage, formation of the second generation of arms (primary alkoxide anions).

polymer with 20 arms, then $[\eta]$ would be close to 17, not far from our value of 15.5.

Acknowledgment. This work was supported financially by the Polish State Committee for Scientific Research (KBN) Grant No. 3 T09A 071 16.

References and Notes

(1) Lapienis, G.; Penczek, S., inventors for Polish Academy of Science. Pol. Pat. Appl. 1998 (tentative number P-328117).

(2) Communications and posters presented at Annual Symposia of the Polish Chemical Society: (a) Lapienis, G.; Penczek, S. Gdansk, Poland, 1997. (b) Lapienis, G.; Biela, T. Wroclaw, Poland, 1998. (c) Lapienis, G. Rzeszow, Poland, 1999.

(3) Biela, T.; Lapienis, G.; Penczek, S. Communication presented at the Europolymer Conference 1999 (EUPOC'99), Gargnano, Italy.

(4) (a) Zilliox, J. G.; Rempp, P.; Parrod, J. *J. Polym. Sci.* **1968**, *C22*, 145. (b) Worsfold, D. J.; Zilliox, J. G.; Rempp, P. *Can. J. Chem.* **1969**, *47*, 3379.

(5) Rempp, P.; Lutz, P.; Franta, E. *J. Macromol. Sci.—Pure Appl. Chem.* **1994**, *A31*, 891.

(6) Rempp, P.; Lutz, P. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; Vol. 10, p 7880.

(7) Marsalkó, T. M.; Majoros, I.; Kennedy, J. P. *Polym. Bull.* **1993**, *31*, 665; *Macromol. Symp.* **1995**, *95*, 39.

(8) Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1991**, *24*, 2309, 5741.

(9) Gnanou, Y.; Lutz, P.; Rempp, P. *Makromol. Chem.* **1988**, *189*, 2885.

(10) Taton, D.; Cloutet, E.; Gnanou, Y. *Macromol. Chem. Phys.* **1998**, *199*, 2501.

(11) Emrick, T.; Chang, H.-T.; Frechet, J. M. J. *Macromolecules* **1999**, *32*, 6380.

(12) Tokar, R.; Kubisa, P.; Penczek, S.; Dworak, A. *Macromolecules* **1994**, *27*, 320.

(13) Sunder, A.; Mülhaupt, R.; Frey, H. *Macromolecules* **2000**, *33*, 309.

(14) (a) Haines, A. H. in *Comprehensive Organic Chemistry*; Stoddart, J. F., Ed.; Pergamon Press: Oxford, England, 1979; Vol. 1, p 853. (b) Gritter, R. J. In *The Chemistry of the Ether Linkage*; Patai, S., Ed.; Interscí Publ.: London, 1967; Chapter 9, p 373.

(15) Lapienis, G.; Penczek, S. Manuscript in preparation.

(16) Comanita, B.; Noren, B.; Roovers, J. *Macromolecules* **1999**, *32*, 1069.

MA000115N