Macromol. Symp. ***195****, 317–327 (2003)*

Multibranched Star-Shaped Polyethers

*Grzegorz Lapienis, Stanislaw Penczek**

Department of Polymer Chemistry, Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90-363 Lodz, Sienkiewicza 112, Poland
E-mail: spenczek@bilbo.cbmm.lodz.pl

Summary: Synthesis of multibranched star-shaped polyethers having poly(ethylene oxide)s (PEO) arms is described. The novel method of preparing these multibranched macromolecules consists in reaction of the -OH ended oligomers with dicyclic compounds; e.g. monoalkyl ethers of poly(ethylene oxide) with diepoxides in the presence of a basic catalyst, converting a part of the ~OH groups into $\sim O^{\sigma}$ end groups (alkoxide anions). Analysis of the structure of these macromolecules was mostly based on ^{1}H NMR, MALDI-TOF, and SEC with triple detection. The absolute values of M_w (LS), M_w/M_n and $[\eta]$ are given, indicating formation of macromolecules of high molar mass and highly branched. The number of branches was estimated by several methods, including comparison of the Mark-Houwink (M-H) dependencies of the obtained products with the M-H dependence for PEO stars with exactly known number of arms. The final stars were phosphorylated at the –OH ended branches. Almost exclusively monoesters of phosphoric acid were found in ^{31}P (^{1}H) NMR.

Keywords: anionic polymerization; NMR; poly(ethylene oxide); size exclusion chromatography (SEC); star polymers

Introduction

In our preliminary paper related to the new method of formation of star-shaped highly branched macromolecules, we gave a short description of this novel and general approach.[1a] This approach is an extension to cyclic compounds of the already known method, used with unsaturated compounds and based on the reaction of difunctional monomer (thus, giving linear chains) with tetrafunctional monomer (giving by itself networks). The best known is polymerization of styrene in the presence of divinylbenzene (DVB)[2-4] or 1.4 butadiene[5,6] in the presence of DVB. Since then, there was a large number of similar syntheses, mainly involving methacrylates,[7,8] vinyl ethers[9] or isobutene.[10]

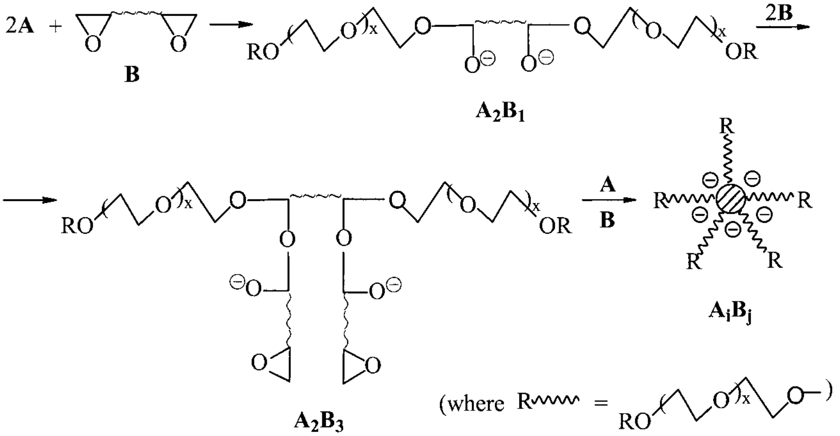
In 1976 one of us (S.P.) published a paper, describing polymerization of cyclic acetals in the presence of diepoxides.[11]. However, at that time there was no attempt to characterize the resulting products and even the expressions “star” or “highly branched” were not used for thus emerging macromolecules.

The reaction scheme for our method (following the cited short communication[1a]) looks as follows:

1st Stage: formation of the first generation of arms (in case of PEO)

(1)

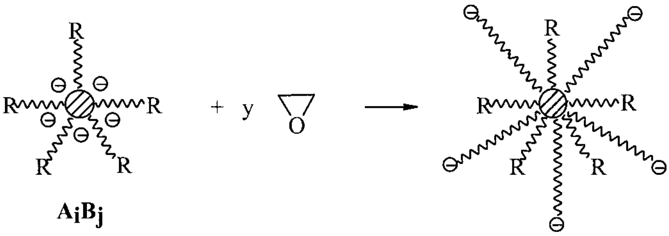
2nd Stage: formation of reactive core fitted with arms and alkoxide anions, as a result of a series of the parallel-consecutive reactions:



(2)

(and where $\mathbf{A_iB_j}$ is the first star with *i* arms and *i* alkoxide anions on the core)

3rd Stage: formation of the second generation of arms (second star)



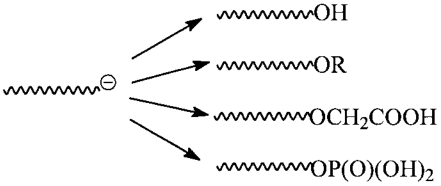
(3)

first star

second star with *i* first arms and at least *i* second arms fitted with $-OCH_2CH_2OH$ and/or $-OCH_2CH_2O^{\sigma}$ end-group.

4th Stage: functionalization

e.g.



(4)

Scheme 1

Reactions 1-4 shown in Scheme 1 were carried on in THF at 25°C.

Stars with phosphorylated end groups were successfully prepared in a clean process of a direct phosphorylation with $POCl_3$.

Results and Discussion

Precursors of the first arms in the present work were of two origins: either ethylene oxide (EO) was polymerized anionically, mostly with t-butoxycesium and then used as such (an aliquot was taken for analysis) or commercial monomethyl ether of poly(ethylene glycol) (MPEG) was converted fully or partially into its anions. Starting MPEG's were purified (from PEG) by elaborated by us chromatographic method.[12] This method gives MPEG with a content of PEG reduced below 1%; this is also a threshold of the analytical methods applied.[12]

Observation of Steps 1, 2, 3 and 4 by ^{1}H and ^{31}P NMR

Step 1. As shown in Table 1 the calculated M_n of the precursors agree with M_n as determined by three different methods (^{1}H NMR from two end groups, SEC and MALDI-TOF-ms). In three experiments with precursors of calculated M_n 2340, 3360, and 3050, the corresponding respective values of determined M_n (average of several measurements of Table 1) were observed: 2265, 3390, and 3190.[13]

In the ^{1}H NMR spectra of precursor macromolecules (oligomers) capped with trifluoroacetic anhydride, exclusively esters of primary alcohols, $-\underline{CH_2}OC(O)CF_3$ (δ= 4.5 ppm) are observed. The electronic integration of the tail ($-\underline{CH_2}OC(O)CF_3$) and head ($(\underline{CH_3})_3C-$) end groups agree well (expt. 2:8.88; calcd.2:9.0).[1a]

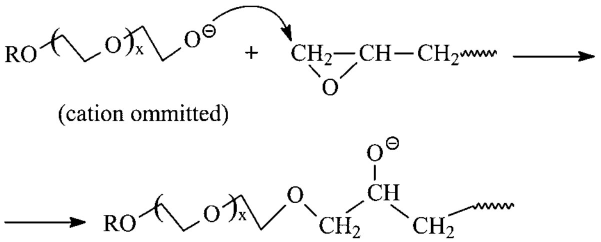
Table 1. Analysis of precursors[13] (data partly from our earlier works[1a, 12a]).

No.	M_n								
	Calcd.	^{1}H NMR (end-groups)		SEC d)			MALDI-TOF		
		t-BuO-	$-CH_2OH$ e)	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n
1	2340 a)	2230	2220	2530	2790	1.10	2077	2147	1.03
2	3360 a)	3810	3210	3270	3330	1.02	3257	3348	1.03
3	3050 a)	3420	3170	2990	3200	1.07	3168	3223	1.02
4	550 b)	494 f)	472	(365)	(474)	(1.30)	517	562	1.09
5	2000 c)	2100 f)	2105	(2170)	(2440)	(1.12)	1975	2012	1.02

a) polymerization of EO initiated with t-BuOK; r.t., in THF solution
b) nominal M_n of MPEG 550
c) nominal M_n of MPEG 2000
d) 3 columns Suprema (PSS); Viscotek: triple detections; in brackets values from calibration on PEG standards
e) determined after addition of $(CF_3CO)_2O$
f) determination from CH_3O- end-group

Step 2. Formation of the "first star".

According to Scheme 1, in formation of the first stars the following two major reactions take place:

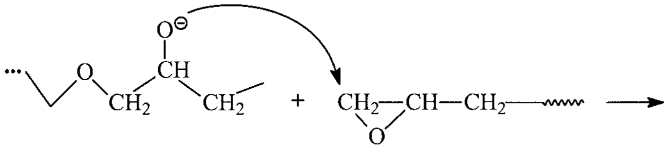


(cation ommitted)

(5)

(mostly ∀ opening; i.e. attack on the least substituted carbon atom; conversion of the primary to the secondary $-O^{\sigma}$ (-OH) is usually taking place)

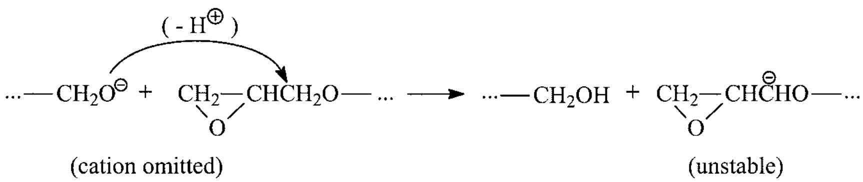
and



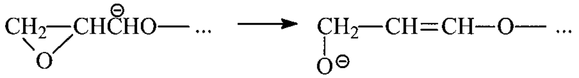
(6)

→ mostly α- opening; reformation of the secondary $-O^{\ominus}$ alkoxides: $-O^{\ominus}$(-OH)

Indeed, in this first stars only trifluoroacetates of secondary alcohols ($>\underline{CH}OC(O)CF_3$; δ= 5.3 ppm) were observed. Integration gives however the ratio of protons from two end groups, namely $>C\underline{H}O$- and $(C\underline{H}_3)_3CO$- 1:6 in place of 1:9, when $(C\underline{H}_3)_3CO^{\sigma}$ initiator was used. This may mean that at this stage the total number of active sites, i.e. alkoxide anions and –OH groups increases. The most probable reason is chain transfer, known in polymerization of substituted oxiranes (e.g. in polymerization of methyloxirane[14,15]). Thus, we assume that following sequence of reactions takes place:



(7)


(8)

Thus formed allyloxy unit is already on the core and its further fate is not certain. It may either enter the sequence of reactions 1-3 (Scheme 1) or it may stay as such, if epoxy groups are already consumed. Concentration of allyloxy units may be low and therefore not detectable by methods we have used. Nevertheless, in our further calculations and analysis of the number of arms we assumed that the number of the second generation of arms (formed in the third step; Scheme 1) is by a factor 1.5 higher than the number of arms formed in the second step (first generation).

The ^1H NMR spectra of the reaction products are taken during the first star formation; i.e. when epoxy groups are still present and after reaction is completed (Figure 1). The fragment of the spectrum related to the epoxy groups absorption is expanded.

On the basis of a number of spectra, from which concentrations of epoxy groups were determined, it was possible to determine the apparent (total) rate constant of reaction of epoxy groups with hydroxyl groups. This rate constant is a function of 8 rate constants, namely rate constants of reactions 9-12 (i.e. of reactions of primary and secondary –OH and/or $-O^{\sigma}$ with methylene and methine groups in epoxy structure).

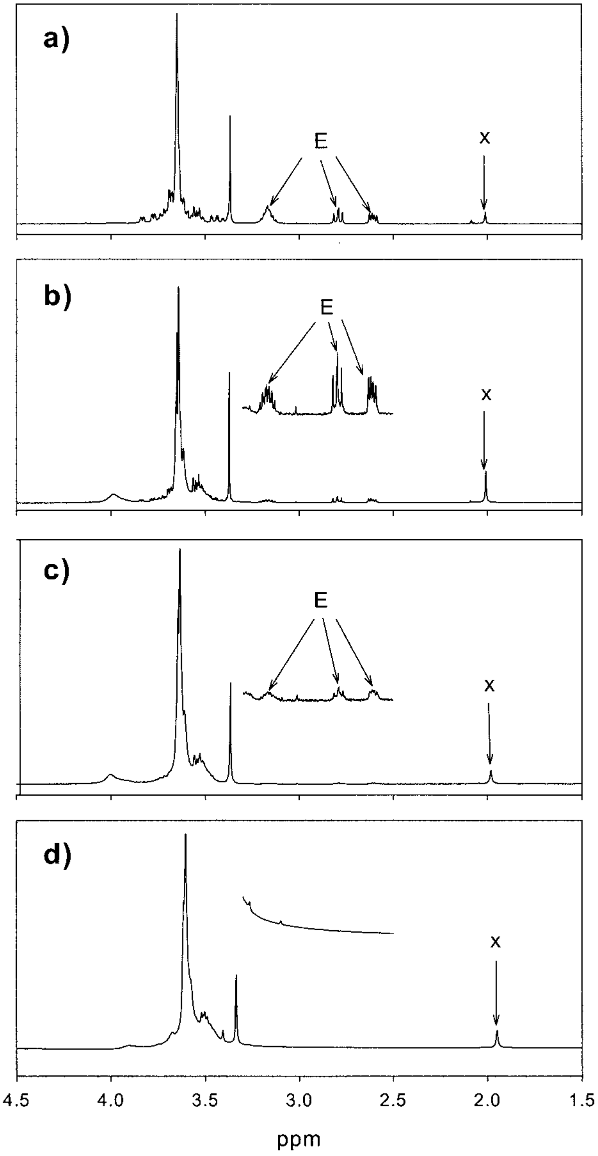
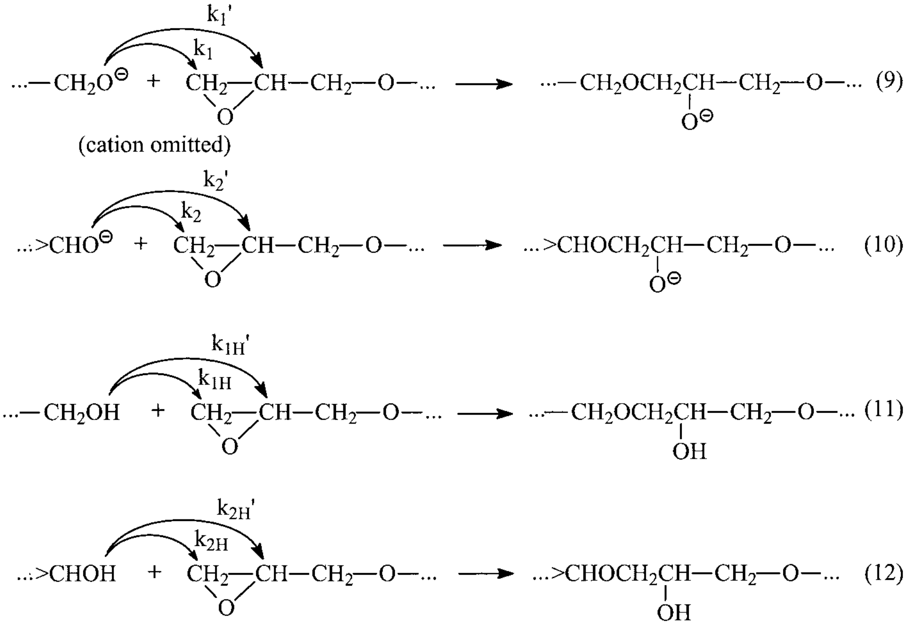


Figure 1. ^{1}H NMR spectra of the reaction mixture (in $CDCl_3$) during the II stage of the reaction between MPEG 296 and diglycidyl ether of ethylene glycol (DGEEG) in bulk at 60°C; [DGEEG]/[MPEG 296] = 0,92; [RONa]/[ROH] = 46,7%. The spectra relate to 0 min (a), 45 min (b, 32.5% of epoxy groups are still present), 120 min (c, 17.0% of epoxy groups are still present), and 275 min (d, the end of reaction; epoxy groups could not be determined). Inserted fragments of the spectra in the range of the epoxy groups absorption are magnified 10 times; E - signals derived from epoxy groups; x - residue of CH_3COOH. [13]

The following kinetic scheme has been considered:



Scheme 2

Presumably the rate of reaction with -O$^{\sigma}$ is much higher than with –OH, therefore we should consider only four rate constants of individual reactions; thus the measured $k^*_{app} = \alpha(k_1 + k_1')$ $+ (1-\alpha)(k_2 + k_2')$, where α is a proportion of primary -O$^{\sigma}$, given by $-O^{\sigma}_{(pr)}/(-O^{\sigma}_{(pr)} + -O^{\sigma}_{(sec)})$. It has been reported that the presence of hydroxy groups in the reaction mixture lowers the rate of polymerization of ethylene oxide (EO)[16] and propylene oxide (PO).[17] In the case of EO the propagation rate constant at 80°C on the alkoxide ion-pair is lower in the presence of an alcohol more than 10^3 times than on ion-pair in the absence of hydroxyl groups.[16]

There is no direct access to α, since the ratio $-OH_{(pr)}/-OH_{(sec)}$ that is known after "killing" the corresponding anions is not necessarily equal to the $-O^{\sigma}_{(pr)}/-O^{\sigma}_{(sec)}$ during the reaction. Nevertheless, the k_{app} values give a certain measure of the total rate of reaction for alkoxy anions with epoxy groups in these systems.

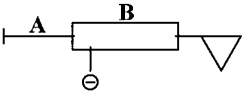
We have assumed that both $k_1 > k_1'$ and $k_2 > k_2'$. This is justified, again on the basis of the abundant literature data, giving mostly the ratio of two constants from the determined ratio of the corresponding products. It has been reported, on the bases of the analysis of ^{13}C NMR spectra of poly(propylene oxide) (PPO), that during polymerization of PO approx. 3 % of additions occur at 80°C by attack at tertiary carbon.[15,18,19] That means that the rate constant k_1 is approx. 30 times higher than k_2. According to our estimated values the ratio of k_1/k_2 is equal to 5 at 60°C. The apparent rate constants were calculated: $k_1 = 3.12 \cdot 10^{-4}$ L/(mol·s) and $k_2 = 6.31 \cdot 10^{-5}$ L/(mol·s) ([DGEEG]/[MPEG 296] = 0.92, bulk, $\text{-O}^{\sigma}/\text{-OH} = 0.47$, 60°C). Any comparison with k_p known in polymerization of e.g. propylene oxide (the closest structure) are difficult, since ions and ion pairs participate simultaneously and their proportions are not known. Since in bulk, however, the dissociation constant is very low, we could compare our results (presumably $k_p^{\pm}$) with $k_p^{\pm}$ in propylene oxide polymerization in bulk at 60°C. The reported value was $1.2 \cdot 10^{-4}$ L/(mol·s),[20] not too far from our result.

MALDI-TOF-MS Analysis of Stars

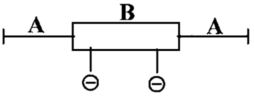
MALDI-TOF-ms allowed observing individual products of reaction. In the majority of experiments MPEG used was not an individual compound. Therefore, the MALDI-TOF mass spectra show two superimposed distributions. Distribution of the molar masses of the stars formed and within each product an additional distribution of arms. These spectra are becoming even more complicated when stars of the second generation are analysed. However, much simpler spectra appear when individual MPEG is taken for reaction. An oligomer of the MPEG structure of the highest molar mass that we were able to purify by distillation of commercial MPEG 350 was monomethyl ether of hexa(ethylene glycol) with molar mass equal to 296.

From MALDI-TOF mass spectra, when monomethyl ether of hexa(ethylene glycol) (**A**) was used as a model compound in the reaction with diglycidyl ether of neopentyl glycol (NP) (**B**) we were able to observe individual products of addition of the general formula $\mathbf{A_iB_j}$. Thus, the first formed $\mathbf{A_1B_1}$, then $\mathbf{A_2B_1}$ etc. It is interesting to note, that there are two clearly separated distributions of products, namely having an even number of **A** and **B** and uneven number. The first members of these two populations can be visualized as follows:

$\mathbf{A_1B_1}$:



and $\mathbf{A_2B_1}$



(where ▽ is an unreacted epoxy group)

In every product with even (**A_1B_1**; **A_1B_3**; **A_2B_2** etc) number of components (provided that number of components **B** is equal or larger than the number of components **A**) two different reacting groups are present, the alkoxide anion and epoxy group, whereas in the uneven (odd) category there are exclusively alkoxide anions. Thus, the probability of reaction is higher for the former category.

On the basis of analysis of the distribution of products observed by MALDI-TOF-ms it was not possible, at the present time, to estimate values of k_1 and k_2 (Scheme 2), since the dependence of response on the structure is not known.

Number of Arms

The simplest way to determine the number and weight average number of arms is based on a simple determination of the absolute molar masses. Since M_n and M_w are known for precursors of the first arms, the values of f_n and f_w are simply computed by using the following formulae:

$$f_n = M_{n,star} \cdot (1 - w_{core})/M_{n,arm} \tag{13}$$

$$f_w = M_{w,star} \cdot (1 - w_{core})/M_{n,arm} \tag{14}$$

M_n and M_w of stars were determined with the triple detection Viscotek apparatus. The required values of *dn/dc* were either taken directly as an average value, determined by Viscotek from SEC slices, or determined independently. The difference between these two determinations were not larger than 20 % of the measured value. Therefore, for a large majority of our measurements we simply used the Viscotek's data. The obtained stars have up to 50 arms.[13]

Fortunately, there are also data of Roovers[21] available, who determined the Mark-Houwink plots (dependence of $[0]$ on M_w) for PEO stars with a known number of arms f, equal to 4, 8 and 16. Therefore, we could use these plots for our data, having f, M_n, M_w, and $[0]$ for a given sample. In order to put our points on the Roovers' plot we could only use stars with not too large M_w/M_n ratio, in order not to take any arbitrary value of a molar mass. Thus, we put on the Roovers' graphs both M_n and M_w for a given value of $[0]$ and then compare the value of f_n, determined from $M_{(star)}/M_{(arms)}$ with the corresponding value of f, resulting from the Roovers' plots. Taking into account the fact, that our stars have cores that substantially differ from these in the Roovers' stars, the difference of 1.5 to 2.0 times between f_n determined as $M_{(star)}/M_{(arms)}$ and f from the Roovers' plots seems satisfactory, indicating that our procedures of calculations were correct.[13]

Functionalization of the High Molar Mass Star-Shaped PEO

The resulting branched macromolecules were terminated with different reagents (4th stage in Scheme 1): (a) CH_3COOH/CH_3OH → -OH; (b) RBr → -OR; (c) $BrCH_2COOH$ → $-OCH_2COOH$; (d) $POCl_3$ → $-OP(O)(ONa)_2$. In each case a large excess of reagent was introduced to the reaction mixture. In the case of $-OP(O)(ONa)_2$ as end-groups, 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, Figure 2). 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.

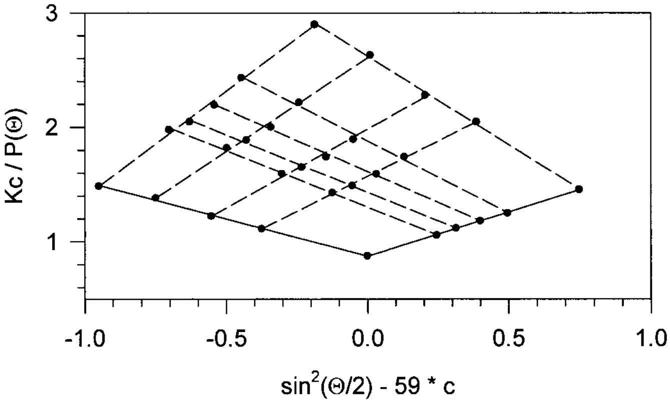


Figure 2. Zimm plot of phosphorylated star-shaped polymer.

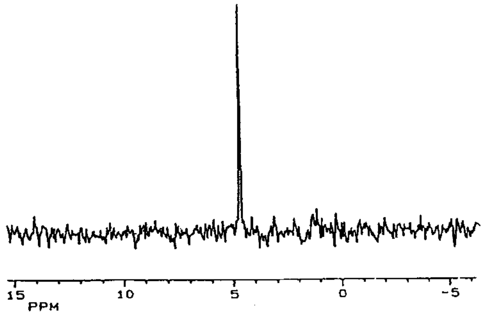


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of phosphorylated star-shaped polymer.

In the $^{31}P\{^{1}H\}$ NMR spectrum (Figure 3) only one signal at $\delta = 4.73$ ppm was observed, thus exclusively monoesters of H_3PO_4 are present.[1a] A large excess of $POCl_3$ over –OH groups was used.

Acknowledgement: This work was partially supported financially by the Polish State Committee for Scientific Research (KBN) grants No. 3 T09A 071 16 and 7 T09A 156 21.

[1a] G. Lapienis, S. Penczek, *Macromolecules* **2000**, *33*, 6630.
[1b] Pol. Pat. Appl. 1998 (tentative number P-328117), invs.: G. Lapienis, S. Penczek.
[2] J. G. Zilliox, P. Rempp, J. Parrod, *J. Polym. Sci.* **1968**, *C22*,145.
[3] P. Rempp, P. Lutz, E. Franta, *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31*, 891.
[4] P. Rempp, P. Lutz, in: *"Polymeric Materials Encyclopedia"*, J. C. Salamone, Ed., CRC Press, Inc., Boca Raton 1996, Vol. 10, p. 7880.
[5] G. Quack, L. J. Fetters, N. Hadjichristidis, R. N. Young, *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 587.
[6] N. Young, L. J. Fetters, *Macromolecules* **1978**, *11*, 899.
[7] Z. Zhu, J. Rider, C. Y. Yang, M. E. Gilmartin, G. E. Wnek, *Macromolecules* **1992**, *25*, 7330.
[8] A. Simms, H. J. Spinelli, in *"Macromolecular Design of Polymeric Materials"*, K. Hatada, T. Kitayama, O. Vogl, Eds., Marcel Dekker 1997, p. 379.
[9] S. Kanaoka, M. Sawamoto, T. Hashimura, *Macromolecules* **1991**, *24*, 2309, 5741.
[10] T. M. Marsalkó, I. Majoros, J. P. Kennedy, *Polym. Bull.* **1993**, *31*, 665; *ibid. Macromol. Symp.* **1995**, *95*, 39.
[11] J. Feigin, S. Penczek, M. Tomaszewicz, *Polimery* **1976**, *21*, 446.
[12a] G. Lapienis, S. Penczek, *J. Bioactive Compatibl. Polym.* **2001**, *16*, 206.
[12b] Pol. P-178 037 (1994), invs.: S. Penczek, G. Lapienis.
[13] G. Lapienis, S. Penczek, in preparation
[14] F. C. Schilling, A. E. Tonelli, *Macromolecules* **1986**, *19*, 1337.
[15] F. Heatley, J. Ding, G. Yu, C. Booth, *Makromol. Chem., Rapid Commun.* **1993**, *14*, 819.
[16] K. S. Kazanskii, A. A. Solov'anov, *Vysokomol. Soedin., Ser. B* **1977**, *19*, 498.
[17] N. P. Doroshenko, Yu. L. Spirin, *Vysokomol. Soedin., Ser. A* **1970**, *12*, 2481.
[18] F. Heatley, Y.-Z. Luo, J.-F. Ding, R. H. Mobbs, C. Booth, *Macromolecules* **1988**, *21*, 2713.
[19] G.-E. Yu, A. J. Masters, F. Heatley, C. Booth, T. G. Blease, *Makromol. Chem. Phys.* **1994**, *195*, 1517.
[20] J. Ding, C. Price, C. Booth, *Eur. Polym. J.* **1991**, *9*, 891.
[21] B. Comanita, B. Noren, J. Roovers,. *Macromolecules* ,**1999**, *32*, 1069.