Macromolecules **2000,** 33, 315−320

Functional Poly(ethylene oxide) Multiarm Star Polymers: Core-First Synthesis Using Hyperbranched Polyglycerol Initiators

Ralf Knischka and Pierre J. Lutz*

Institut Charles Sadron, (CNRS), 6, rue Boussingault, F-67083 Strasbourg Cedex, France

Alexander Sunder, Rolf Mülhaupt, and Holger Frey*

Institut für Makromolekulare Chemie und Freiburger Materialforschungszentrum FMF der Albert-Ludwigs-Universität, Stefan-Meier-Str. 21/31, D-79104 Freiburg, Germany

Received July 20, 1999; Revised Manuscript Received October 26, 1999

ABSTRACT: Hyperbranched polyglycerol as well as polyglycerol modified with short apolar oligo(propylene oxide) segments ($DP_n = 23-52$; $M_w/M_n = 1.2-1.4$) was deprotonated with diphenylmethylpotassium and used as polyfunctional initiators for the anionic polymerization of ethylene oxide to prepare poly(ethylene oxide) (PEO) multiarm star polymers. In the case of unmodified polyglycerol, after metalation, aggregation occurred, preventing efficient initiation and propagation. Using the apolarly modified polyglycerols with terminal oligo(propylene oxide) segments, hydroxyfunctional PEO multiarm star polymers with M_n values in the range 34 000−95 000 g/mol, arm numbers in the range 26−55, and narrow polydispersity ($M_w/M_n < 1.5$) were obtained in a core-first strategy. ^{1}H and ^{13}C NMR measurements evidenced complete conversion of all end groups of the propylene oxide-capped end groups of the initiator. Reinitiation of the multiarm PEO stars by deprotonation was possible and afforded star polymers with considerably larger molecular weights (M_n = 180 000 g/mol) and identical functionality. The thermal properties of the stars (DSC) were found to depend strongly on the arm length. The novel multiarm star architectures prepared consist of polyether structures only and are thus of interest for biomedical applications, e.g., in hydrogels.

Introduction

Multiarm star polymers are three-dimensional macromolecules, in which a large number of linear arms of similar molecular weight and narrow molecular weight distribution emanate from a central core.[1] This class of star polymers recently attracts increasing interest due to the compact structure, which may lead to peculiar rheological properties.[2] In addition, end-functional multiarm star polymers possess unusually high functionality that permits further modification or cross-linking.[3]

Functional poly(ethylene oxide) (PEO) star polymers are regarded as a particularly promising class of materials, since they represent variable building blocks for structured polymer networks, e.g., hydrogels[4] or amphiphilic network systems.[5] Due to the excellent biocompatibility of PEO, both the star precursors and the resulting networks are of interest for biomedical and pharmaceutical applications. In this context, Merrill et al. recently demonstrated that due to their high functionality PEO stars attached to a surface permit size-selective protein adsorption.[6]

Generally, star polymers can be prepared by two different routes: the “arm-first”[7−10] strategy and the “core-first”[11,12,15] approach on the basis of a multifunctional core used as initiator. In the latter case the arm length can be tailored by the ratio of active sites to the amount of added monomer. Well-defined PEO star polymers with three or four arms have been obtained in a core-first manner on the basis of trimethylolpropane or pentaerythrol cores, respectively. For the synthesis of PEO multiarm stars with considerably higher functionality, the core-first method employing a poly(divinylbenzene) core (DVB) is now commonly used.[13] The main disadvantage of the materials obtained by this procedure is the relatively large polydispersity both concerning molecular weights of the arms as well as functionality. This leads to undesired aggregation in aqueous media or in methanol because of insufficient shielding of the apolar hydrocarbon cores by PEO chains,[14] which induces amphiphilic properties of the resulting stars. An improved route along this line has been presented recently, based on a poly(1,3-diisopropenylbenzene) core, permitting better control of the functionality.[15]

A novel route toward PEO multiarm stars based on dendrimers was presented in recent elegant work by Merrill et al.[9] as well as by Roovers et al.,[16] using poly(amidoamine) (PAMAM; arm-first) as well as carbosilane dendrimers (core-first) with functional end groups as core molecules, respectively. In these works, the number of PEO chains per star molecule was as high as 32.[9] However, a drawback of this route lies in the tedious preparation of the dendrimer core molecules, which has to be carried out in a multistep synthesis.[17] An alternative strategy for the preparation of multiarm star polymers has been introduced recently, which relies on the use of hyperbranched[18−20] polyester core molecules. Unfortunately, hyperbranched polymers usually exhibit broad polydispersity, limiting the potential of this method for the preparation of well-defined stars. Furthermore, polyester structures are not stable under the conditions of the living anionic polymerization of ethylene oxide.

In a recent publication, we described the controlled synthesis of hyperbranched polyglycerol, based on the anionic ring-opening multibranching polymerization (ROMBP) of glycidol.[21] This route permits to tailor the degree of polymerization ($DP_n = 15-100$) and leads to polydispersities below 1.5 (mostly below 1.3). In subsequent work, we have been able to demonstrate that the

10.1021/ma991192p CCC: $19.00 © 2000 American Chemical Society
Published on Web 12/29/1999

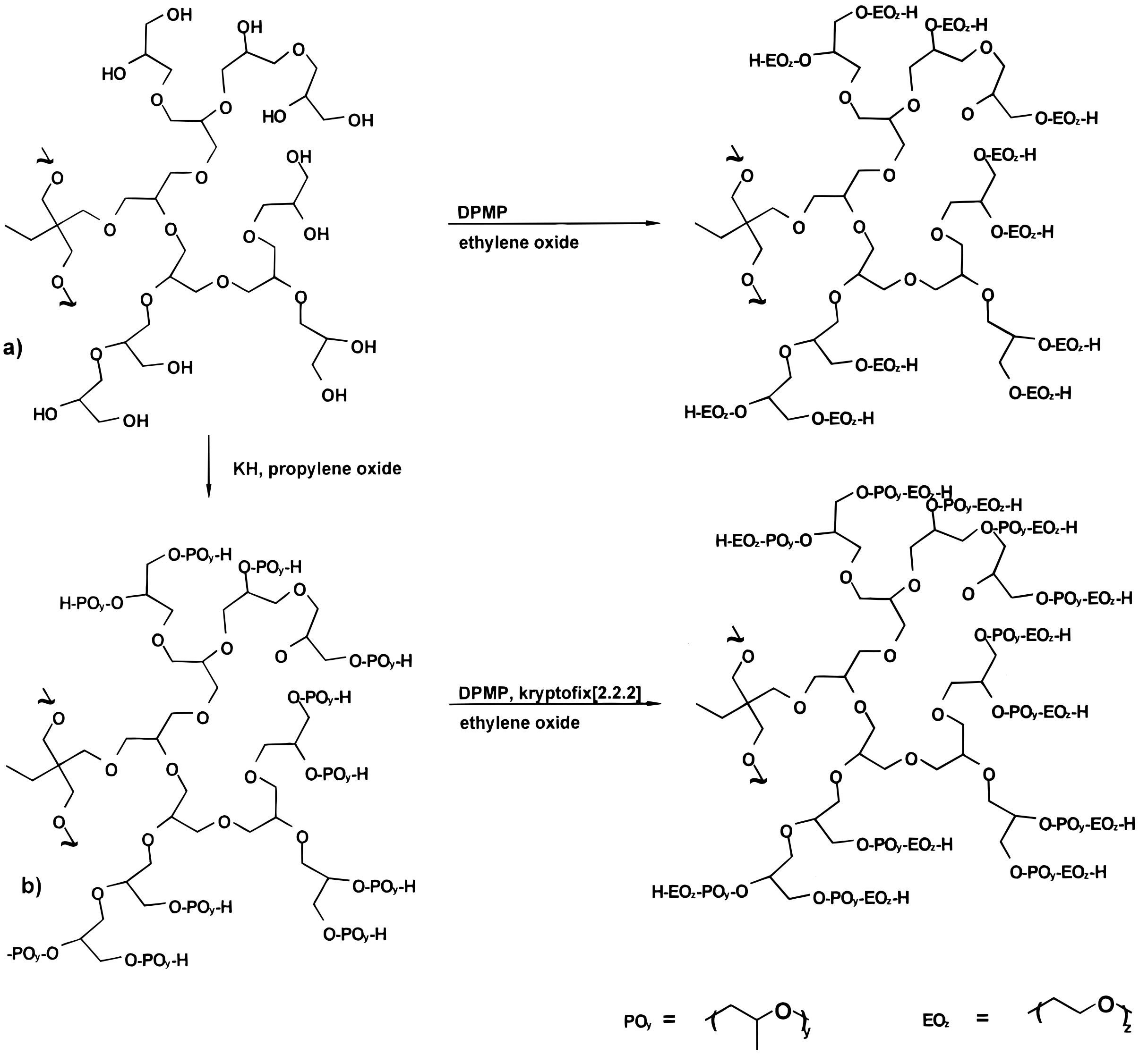

Figure 1. Synthesis of poly(glycerol-*b*-ethylene oxide) and poly(glycerol-*b*-propylene oxide-*b*-ethylene oxide) starting from a polyglycerol (a) or poly(glycerol-*b*-propylene oxide) (b), respectively.

solubility limitations of the highly polar hyperbranched polyglycerol can be overcome by the attachment of several propylene oxide units to the polyglycerol end groups, permitting control of the polarity of the hyperbranched structure without variation of the overall functionality.[22]

In the current paper we wish to describe a novel approach to PEO multiarm stars consisting of polyether structures only, using the well-defined polyglycerols as polyfunctional initiators in a core-first strategy. The synthetic route is illustrated in Figure 1. Both polyglycerol and the propoxylated polyglycerols were employed as polyfunctional initiators. The resulting materials are discussed with respect to achievable molecular weights, polydispersities, and thermal as well as dilute solution properties.

Experimental Section

Materials. Ethylene oxide was purchased from Fluka, degassed, distilled twice over sodium wire, and stored in graduated Schlenk vessels. THF and DMSO were carefully dried using standard procedures. Polyglycerol,[21] propoxylated polyglycerols,[22] and kryptofix [2.2.2] were extensively dried under high-vacuum conditions at elevated temperatures. Diphenylmethane and naphthalene were used as purchased.

Synthesis. Diphenylmethylpotassium was synthesized according to well-known procedures in THF solution.

Poly(glycerol-b-ethylene oxide). Poly(glycerol-*b*-ethylene oxide) was prepared in DMSO or DMSO/THF (1/4), respectively. Polyglycerol was dried in high vacuum at 60 °C for 24 h in the reaction vessel. A five-necked round-bottom flask equipped with argon inlet, graduated ethylene oxide ampule, and initiator buret was used. DMSO or DMSO/THF was then added, and the metalation up to a degree of 25% was carried out with diphenylmethylpotassium at 50 °C. A slight vacuum was applied, and the calculated amount of ethylene oxide was added at −40 °C. Subsequently, the system was heated to 30 °C under stirring. The polymerization was carried out for several days. The reaction was terminated by addition of a drop of acidified MeOH. The solution was centrifuged to remove KCl and possible gel fractions, subsequently precipitated twice in diethyl ether, and the product was dried.

Poly(glycerol-b-propylene oxide-b-ethylene oxide). Poly(glycerol-*b*-propylene oxide-*b*-ethylene oxide) was prepared in THF. Poly(glycerol-*b*-propylene oxide) and kryptofix [2.2.2] were dried under high vacuum at 60 °C for 24 h. THF was added, and the metalation of 25% of the hydroxyl groups was carried out with diphenylmethylpotassium at 50 °C. A slight vacuum was applied, and about 2 mL of ethylene oxide was added at −40 °C. The system was heated to 50 °C for about 1 h, and after that the remaining quantity of ethylene oxide was added at −40 °C. The polymerization was carried out at 35 °C for

Table 1. Characterization Data for Polyglycerol and Poly(glycerol-*b*-propylene Oxide) Core and Respective Multiarm Star Polymers

sample	core unit	PD_{core}	M_n (calcd)[a]	M_n (branch)[b]	M_n (SEC)[c]	PD_{star}	yield [%]
$P(G_{39}EO_{20})$	PG_{39}	1.3	40 000	n.d.	8 000	2.0	95
$P(G_{23}PO_3EO_{30})$	$P(G_{23}PO_3)$	1.2	34 000	1300	35 000	1.4	93
$P(G_{23}PO_3EO_{48})$	$P(G_{23}PO_3)$	1.2	55 000	2100	53 000	1.4	95
$P(G_{52}PO_3EO_{17})$	$P(G_{52}PO_3)$	1.4	58 000	750	51 000	1.5	80
$P(G_{52}PO_3EO_{39})$	$P(G_{52}PO_3)$	1.4	95 000	1700	100 000	2.2	85
$P(G_{23}PO_3EO_{180})$	$P(G_{23}PO_3EO_{30})$	1.4	220 000	7600	180 000	1.4	80

[a] Calculated from the [monomer]/[core] ratio employed. [b] Calculated from the obtained molecular weight from the SEC measurement and the hydroxyl number of the core unit employed. [c] Measured in water with SEC/MALLS detection.

several days (usually 3−5 days), depending on the desired degree of polymerization. Termination was carried out by addition of a drop of acidified MeOH. The solution was centrifuged, precipitated in diethyl ether, purified by precipitation or dialysis, and dried. In the case of purification by dialysis a benzoylated cellulose membrane (Sigma) was used.

Characterization. SEC measurements were carried out in water at concentrations of about 5 g/L. SEC was equipped with multiangle light scattering (MALLS) and refractive index (RI) detector, $dn/dc = 0.136$ mL/g (PEO).

^1H and ^{13}C NMR spectra were recorded in d_6-methanol at concentrations of 50 g/L on a Bruker ARX 300 spectrometer, operating at 300 and 75.4 MHz, respectively.

DSC measurements were carried out on a Perkin-Elmer DSC7 differential scanning calorimeter in the temperature range −110 to 80 °C at heating rates of 5 and 30 K/min. Calibration was carried out with decane.

Viscosities were obtained on a Viscologic T1.1 from SEMA Tech operating at 35 °C in methanol. Huggins and Kraemer plots were used to obtain the intrinsic viscosity.

Results and Discussion

In this study we employ well-defined hyperbranched polyglycerol as well as polyglycerols terminated with several propylene oxide units as multifunctional alkoxide initiators for the anionic ring-opening polymerization (AROP) of ethylene oxide. The polyglycerol samples were obtained by controlled anionic ring-opening multibranching polymerization as described recently.[21] This procedure allows the preparation of hyperbranched polyols with polyether scaffold with 20−80 hydroxyl end groups, showing narrow polydispersity below 1.5 (mostly below 1.3). Deprotonation of these polyglycerols followed by the addition of propylene oxide permits tailoring of the polarity (without variation of the hydroxyl functionality) by "capping" the highly polar structure with short oligo(propylene oxide) segments.[22]

The use of multifunctional alkoxide initiators for the anionic polymerization of ethylene oxide in a core-first approach is generally problematic because of their strong aggregation tendency due to the association of the metalated end groups even in polar solvents. Consequently, there is only limited control over molecular weights, and often broad or even multimodal molecular weight distributions are obtained. However, partial deprotonation of the polyols used as initiators suffices to prepare multiarm structures, since a fast dynamic equilibrium between alkoxide and hydroxyl groups ensures simultaneous initiation of all alkoxide groups.

The functionality of the polyglycerols used as polyfunctional initiators was controlled by varying the degree of polymerization, since on average each monomer in the hyperbranched structure contributes one hydroxyl group.[23] Thus, the total number of hydroxyl groups of the polyglycerol initiators is equal to the degree of polymerization (DP_n) plus the functionality of the initiator employed for the polymerization of glycidol.[21] We use polyglycerols with average hydroxyl functionalities of 26, 39, and 55, with DP_n of 23, 36, and 52, respectively, in the present study (cf. Table 1). In the following, these polyglycerol samples are designated $P(G_x)$, wherein x marks the degree of polymerization.

Because of the low solubility of the highly polar polyglycerols in standard solvents for the anionic polymerization of ethylene oxide (e.g., THF), suitable alternative solvents or solvent mixtures had to be identified. Eventually, DMSO/THF (2/8) as well as pure DMSO were used, in which polyglycerol exhibited excellent solubility. The anionic polymerization of ethylene oxide using unmodified polyglycerol as initiator was carried out at 35 °C. At lower temperature pronounced aggregation was observed. Because of this strong aggregation of the alkoxides even in DMSO it was not possible to obtain metalation degrees (i.e., potassium substitution) exceeding 30% on a reasonable time scale. Only at potassium counterion concentrations in the range of 5% did the system remain completely soluble in DMSO. At this low degree of metalation, however, the polymerization rate of the ethylene oxide polymerization decreased drastically. This is explained by eq 1 describing the polymerization rate:[24]

$$\frac{-d[EO]}{dt} = k'[RO^-][ROH][EO] \qquad (1)$$

Equation 1 shows that the polymerization rate is controlled by the concentration of ethylene oxide as well as the alkoxide and hydroxyl group concentrations. Therefore, a compromise between aggregation and polymerization rate had to be found. We used metalation degrees of 20−30% in all polymerization reactions. The yields of star polymers obtained after the polymerization were quantitative in all cases. However, in both DMSO and DMSO/THF only materials with broad molecular weight distribution and limited molecular weights were obtained. Besides, no control over molecular weights by the ratio EO/polyglycerol initiator was achieved. This is exemplified by the first entry in Table 1 for the sample $P(G_{39}EO_{20})$. Similar results were obtained in a series of polymerization experiments using slightly varied solvent and temperature conditions. Therefore, no further studies with unmodified polyglycerol have been carried out.

To overcome the undesired aggregation effects, polyglycerol samples hydrophobically modified with short oligo(propylene oxide) segments[22] were used for all ensuing polymerizations. Complete propoxylation of all hydroxyl end groups was achieved (^{13}C NMR, vide infra). It should be emphasized that modification with propylene oxide improves the solubility but does not affect the hydroxyl functionality. Also, it is important to note that after "capping" with propylene oxide only secondary hydroxyl groups are present, in contrast to unmodified polyglycerol containing primary as well as secondary OH groups. The propylene oxide terminated polyglycerol initiators are abbreviated P(G_xPO_y) in the following, wherein y marks the number of propylene oxide groups attached (three PO units in the samples employed in this study). The resulting multiarm star PEO polymers are termed P($G_xPO_yEO_z$), z giving the average DP_n of the PEO chains attached to the hyperbranched core.

Similar to the case of the unmodified polyglycerols, we used partial metalation of 25% of the hydroxyl groups of the propoxylated polyglycerols, calculated by the amount of added diphenylmethylpotassium solution. All polymerizations could now be carried out in THF, the initiator remaining soluble even at 25% potassium substitution. Additional use of a cryptate (kryptofix [2.2.2]) led to enhanced reactivity of the alkoxide[25] groups and faster solubilization of the system during chain propagation. This narrows the polydispersities further.[16]

All data obtained (and discussed in detail below) evidence that due to the fast dynamic equilibrium between alkoxides and hydroxyl groups, propagation occurs simultaneously at all chain ends.[26,27] The transformation of a secondary to a primary alkoxide after addition of the first ethylene oxide monomer to the terminal OH groups of the P(G_xPO_y) initiators did not result in inhomogeneous polymerization, as evidenced by ^{13}C NMR spectroscopy discussed below. This is also supported by the narrow molecular weight distributions of the multiarm star polymers. Characterization data of all PEO stars prepared are summarized in Table 1.

The multiarm star polymers were characterized with SEC in water with respect to molecular weights and polydispersity. SEC was equipped with a multiangle light scattering detector (MALLS), and thus the molecular weights measured represent absolute values. The dn/dc for linear PEO was used for the calculations. SEC measurements in THF failed due to the limited solubility of long PEO segments in this medium. Measurements carried out in $CHCl_3$ with polystyrene calibration lead to grossly underestimated values due to the branched, compact structure of the multiarm stars.

In contrast to polyglycerol, the SEC data obtained for the PEO stars show no evidence of aggregation in water, in contrast to the oligo-PO capped polyglycerol core P($G_{23}PO_3$) that strongly aggregates in aqueous media due to the relatively high molar ratio of propylene oxide to glycerol, causing amphiphilic behavior and multimodal molecular weight distributions in SEC.

As exemplified in Figure 2, for all multiarm stars narrow, monomodal molecular weight distributions were obtained. The uncorrected apparent polydispersities were generally in the range 1.4−1.5, with the exception of the highest molecular weight sample P($G_{52}PO_3EO_{39}$) showing an apparent polydispersity of 2.2. The increase of the molecular weights after polymerization of ethylene oxide is clearly visible in Figure 2.

Occasionally, traces of low molecular weight material were observed. This is most probably due to a small quantity of polyglycerol core not incorporated into the star polymer. As demonstrated in Figure 2, this could conveniently be removed for most of the samples either by precipitation in THF/diethyl ether or by dialysis using a modified cellulose membrane with molecular weight cutoff in the range of 25 000 g/mol. For the higher molecular weight samples, generally a shoulder at the low molecular weight side of the distribution was observed that could not be separated, leading to a slight broadening of the molecular weight distribution. This bimodality characteristic for the high molecular weight samples was not observed, when a PEO multiarm star of moderate molecular weight was used as polyfunctional initiator, as detailed in the ensuing paragraph. In summary, SEC evidences that the molecular weights can be controlled reasonably well by the [core]/[ethylene oxide] ratio.

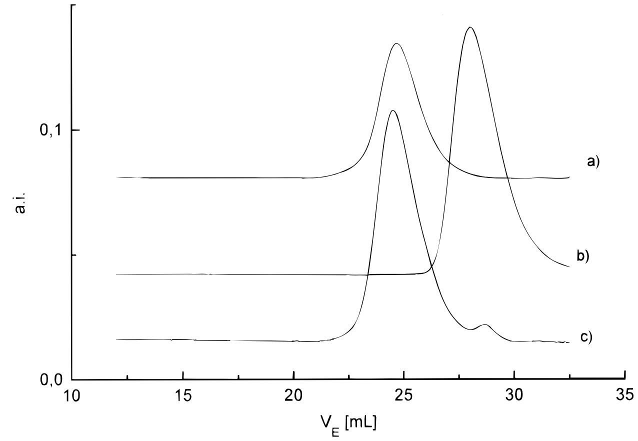

Figure 2. SEC traces of a multiarm star polymer, P($G_{52}PO_3$-EO_{17}) (RI detector): (a) purified product after dialysis, (b) core unit, (c) crude product.

It is well-known that molecular weights of PEO stars attainable by a core-first approach are limited, since the anionic polymerization of ethylene oxide inevitably leads to a broadening of the molecular weight distribution at higher molecular weights. Thus, it is an intriguing issue whether higher molecular weights can be realized by reinitiation of the hydroxy functional multiarm stars. In the present work, we have been able to demonstrate that reinitiation of the multiarm PEO stars by deprotonation is in fact possible and can be employed to prepare PEO stars bearing longer PEO chains. To this end, star P($G_{23}PO_3EO_{30}$) was purified by dialysis, carefully dried, and used as polyfunctional initiator for ethylene oxide, employing a synthetic procedure analogous to the preparation of the multiarm stars described in the previous sections. This approach resulted in a high molecular weight multiarm star P($G_{23}PO_3EO_{180}$) (M_n = 180 000 g/mol), bearing 26 PEO chains with an average DP_n of 180. The polydispersity remained narrow (M_w/M_n = 1.4).

^1H and ^{13}C NMR spectroscopy are valuable methods for the detailed characterization of the novel star architectures, with respect to both the attachment of PEO chains and the confirmation of the SEC results. Therefore, in the following we will discuss representative NMR spectra in some detail. The molecular weights obtained from SEC measurements can be verified by integration of the ^1H NMR spectra, calculating the ratio of the propylene oxide CH_3 protons (1.2 ppm) to the ethylene oxide protons of the PEO main chain. The latter protons show resonances between 3.2 and 3.9 ppm, together with the CH and CH_2 protons of the core. The quantity of propylene oxide per hydroxyl group was obtained from NMR data of the respective initiator employed, as detailed elsewhere.[21,22] The molecular weight values calculated from the ^1H NMR spectra in this manner are in excellent agreement with the ex-

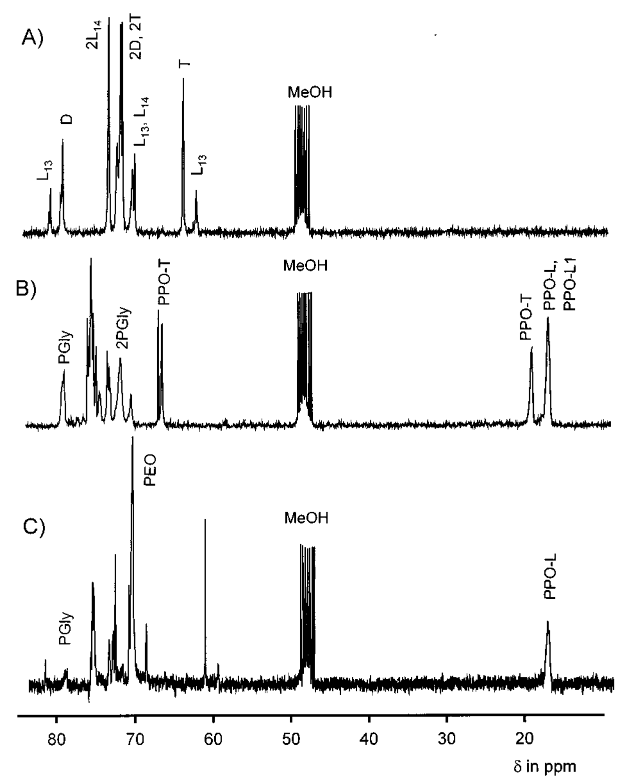

Figure 3. ^{13}C NMR spectra of (a) polyglycerol P(G_{52}), (b) poly(glycerol-*b*-propylene oxide) P($G_{52}PO_3$), and (c) poly(glycerol-*b*-propylene oxide-*b*-ethylene oxide) P($G_{52}PO_3EO_{17}$).

pected values calculated from the [core]/[ethylene oxide] ratio employed as well as the results obtained from SEC/MALLS. The signals of the terminal hydroxyl protons are generally observed at 4.8 ppm in d_4-MeOH.

Figure 3 illustrates the characteristic changes of the ^{13}C NMR spectra before and after modification of polyglycerol with propylene oxide as well as after the final polymerization step. In previous work, all resonances have been assigned unambiguously.[22] Reaction with propylene oxide leads to PPO units incorporated terminally, i.e., as end groups (PPO-T) and linearly (PPO-L) in a ratio of 1:2 for P(G_xPO_3). Subsequent metalation and polymerization of ethylene oxide clearly result in the complete disappearance of the signal of the terminal units (PPO-T), and only signals of propylene oxide incorporated linearly remain. This evidences that all end groups are active in the polymerization process. The addition of one ethylene oxide unit to the poly(glycerol-*b*-propylene oxide) alkoxide then leads to the formation of a primary alkoxide with greatly enhanced reactivity in comparison to the former secondary one. Therefore, it might be argued that the propagation proceeds preferentially at this site, leading to few long chains instead of the desired simultaneous growth of all chains. However, the ^{13}C NMR spectra clearly evidence full conversion of the terminal PO units, since all the signals assigned to the terminal PO group at 20.1 ppm (CH_3), 67.6−68.1 ppm (CH), and 76.0 ppm (CH_2) disappear completely. In summary, ^{13}C NMR spectra unambiguously demonstrate reaction of all terminal PPO units and strongly support simultaneous propagation of all PEO chains.

The solution properties of the PEO stars were investigated at 35 °C by viscosimetry and compared to linear PEO samples (Figure 4). The measurements show a pronounced decrease of the intrinsic viscosity, when comparing linear PEO with the multiarm star polymers, supporting the expected, compact structure of the stars. The [η] values measured for the multiarm stars are listed in Table 2.

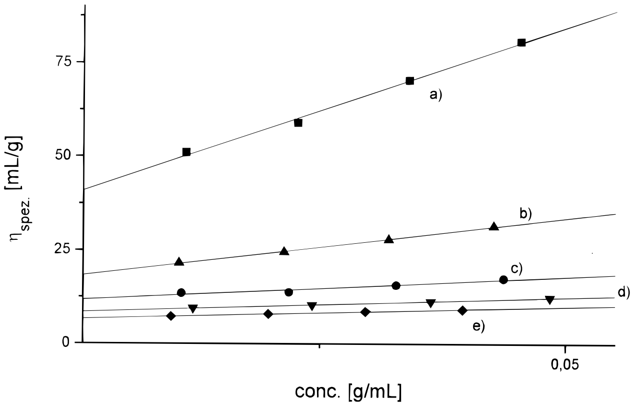

Figure 4. Viscosity data measured in MeOH at 35 °C: (a) PEO linear, M_n = 35 000 g/mol; (b) P($G_{52}PO_3EO_{39}$); (c) P($G_{23}PO_3EO_{48}$); (d) P($G_{23}PO_3EO_{30}$); (e) P($G_{52}PO_3EO_{17}$).

Table 2. Thermal and Dilute Solution Properties of the PEO Multiarm Star Polymers

sample	[η] [mL/g]	T_m [°C]	ΔH_m [J/g]
P($G_{52}PO_3EO_{17}$)	6.6	33	88
P($G_{23}PO_3EO_{30}$)	8.5	44	116
P($G_{23}PO_3EO_{48}$)	10.1	52	133
P($G_{52}PO_3EO_{39}$)	18.1	nd[a]	nd[a]

[a] nd = not determined.

Specific viscosities depending on the arm length as well as arm number, measured at various concentrations, are shown in Figure 4. It should be emphasized that all data exhibit a linear dependence of the specific viscosity on concentration, indicating the absence of aggregation or micelle formation in methanol. It is interesting to note that the viscosimetry data obtained for traditional DVB-core PEO multiarm star polymers in a similar concentration range exhibit different behavior. The DVB-based materials generally show a critical aggregation concentration in MeOH as well as H_2O, which is detectable in all viscosimetry measurements.[28] This is explained by the insufficiently protected hydrocarbon core unit, leading to amphiphilic properties.

Thermal properties of the novel multiarm stars may have some importance for their application and have therefore been investigated using differential scanning calorimetry (DSC). All star polymers show a rather indefinite region between −80 and −10 °C, which does not permit to determine precise glass transition temperatures. This behavior might be explained by the triblock type of structure of the multiarm stars. The melting points, however, of the poly(ethylene oxide) chains of the multiarm stars are clearly visible. Figure 5 shows the respective DSC traces, illustrating the dependence of the melting points on the length of the PEO chains attached. Raising the length of the PEO chains attached from 17 to 39 units causes an increase of the melting temperature from 33 to 52 °C. As expected, the melting enthalpies also increase with increasing arm length. We attribute these trends to a gradually lowered influence of the hydroxyl end groups as well as the noncrystalline polyglycerol core with increasing arm length. Precise measurements concerning the dependence of the crystal structure (SAXS,

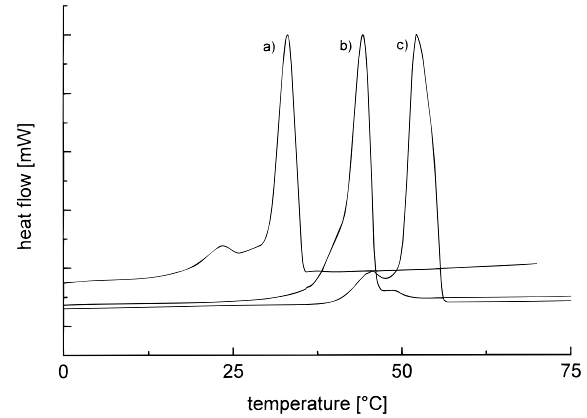

Figure 5. DSC traces for poly(glycerol-*b*-propylene oxide-*b*-ethylene oxide)s differing in arm length and core functionality: (a) P($G_{52}PO_3EO_{17}$), (b) P($G_{23}PO_3EO_{30}$), and (c) P($G_{23}PO_3$-EO_{48}).

WAXS) on the arm length and number as well as the nature of the small endotherm before the actual melting peak are currently in progress. In summary, the data show that variation of the arm length as well as functionality gives the possibility to tailor the thermal properties of the stars.

Conclusion

Hyperbranched polyglycerol as well as polyglycerol modified with short oligo(propylene oxide) segments were employed as polyfunctional initiators for the living anionic ROP of ethylene oxide in order to prepare PEO multiarm star polymers. Whereas unmodified polyglycerol turned out to be unsuitable as initiator due to aggregation effects of the highly polar structure in the solvent combinations tested, apolarly modified polyglycerols with terminal oligo(propylene oxide) segments permitted the synthesis of hydroxyfunctional poly(ethylene oxide) (PEO) multiarm stars with M_n in the range 34 000−95 000 g/mol, chain numbers in the range 26−55, and relatively low polydispersity ($M_w/M_n < 1.5$). Despite a degree of metalation of only 25% and transformation of the secondary hydroxyl groups of propylene oxide end groups into a primary hydroxyl group after initiation, simultaneous propagation at all chain ends occurred, as evidenced by ^{1}H and ^{13}C NMR spectra. The arm length of the obtained PEO stars could be controlled by the [core-OH]/[ethylene oxide] ratio, and excellent agreement between calculated values and molecular weights determined from NMR as well as SEC/MALLS was obtained. Thermal properties of the stars (DSC) were found to depend strongly on the arm length.

Remarkably, reinitiation of the multiarm PEO stars by deprotonation was possible, affording functional PEO multiarm stars with high molecular weights (M_n = 220 000 g/mol).

The novel multiarm star architectures consist of polyether structures only and therefore possess interesting potential for biomedical applications, e.g., in hydrogels or amphiphilic networks. Because of the hydrophilic nature of the polyglycerol core, no aggregation in aqueous media or methanol was observed. This is a main advantage in comparison with the traditional DVB-core route, since the latter synthetic approach leads to a large fraction of apolar hydrocarbon material that makes the materials problematic for biomedical application. Furthermore, the PPO-capped polyglycerols, prepared in a one-pot two-step synthesis, are easily accessible in multigram quantities, which is an important prerequisite for the preparation of these materials on a larger scale. At present, we are investigating the use of the novel multiarm stars for the preparation of structured hydrogels.

Acknowledgment. H.F. thanks the GDCh for financial support in the context of a Hermann-Schnell fellowship.

References and Notes

(1) Meneghetti, S. P.; Lutz, P. J.; Rein, D. In *Star and Hyperbranched Polymers*; Mishra, M. K., Kobayashi, S., Eds.; Marcel Dekker: New York, 1999; p 27.

(2) Blottiere, B.; McLeish, T. C. B.; Hakiki, A.; Young, R. N.; Milner, S. T. *Macromolecules* **1998**, *31*, 9295.

(3) Merrill, E. W. In *Poly(ethylene glycol) Chemistry: Biotechnical and Biomedical Applications*; Harris, J. M., Ed.; Plenum Press: New York, 1992; p 199.

(4) Keys, K. P.; Andreopoulos, F. M.; Peppas, N. A. *Macromolecules* **1998**, *31*, 8149.

(5) Suvegh, K.; Domjan, A.; Vanko, G.; Ivan, B.; Vertes, A. *Macromolecules* **1998**, *31*, 7770.

(6) Sofia, S. J.; Premnath, V.; Merrill, E. W. *Macromolecules* **1998**, *31*, 5059.

(7) Wenger, F.; Yen, S. P. S. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1961**, *2*, 295.

(8) Nguyen, T. G.; Kausch, H. H. *Makromol. Chem.* **1972**, *160*, 213.

(9) Yen, D. R.; Merrill, E. W. *Polym. Prepr. (Am. Chem. Soc.)* **1997**, *38* (1), 531.

(10) Roovers, J.; Zhou, L.; Toporowski, P. M.; Zwan, M.; Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1993**, *26*, 4324.

(11) Lutz, P. J.; Rempp, P. *Makromol. Chem.* **1988**, *189*, 1051.

(12) Eschwey, H.; Hallensleben, M.; Burchard, W. *Makromol. Chem.* **1973**, *173*, 235.

(13) Rein, D.; Lamps, J. P.; Rempp, P.; Lutz, P. J.; Papanagopoulos, D.; Tsitsilianis, C. *Acta Polym.* **1993**, *44*, 225.

(14) Meneghetti, S. P.; Naraghi, K.; Burchard, W.; Lutz, P. J. *J. Int. Symp. Ionic Polym. Paris* **1997**, 348.

(15) Naraghi, K. S.; Plentz Meneghetti, S.; Lutz, P. J. *Macromol. Rapid Commun.* **1999**, *20*, 122.

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

(17) Tomalia, D. A.; Durst, H. D. *Top. Curr. Chem.* **1993**, *165*, 193. Moorefield, F. Vögtle, *Dendritic Macromolecules*: *Concepts, Syntheses, Perspectives*; VCH: Weinheim, Germany, 1996. Matthias, O. A.; Shipway, A. N.; Fraser-Stoddart, J. F. *Prog. Polym. Sci.* **1998**, *23*, 1.

(18) Weberskirch, R.; Hettich, R.; Nuyken, O.; Schmaljohann, D.; Voit, B. *Macromol. Chem. Phys.* **1999**, *200*, 863.

(19) Kim, H. Y.; Webster, O. W. *Macromolecules* **1992**, *25*, 5561.

(20) Hedrick, J. L.; Trollsas, M.; Hawker, C. J.; Atthoff, B.; Claeson, H.; Heise, A.; Miller, R. D.; Mecerreyes, D.; Jerome, R.; Dubois, Ph. *Macromolecules* **1998**, *31*, 8691.

(21) Sunder, A.; Hanselmann, R.; Frey, H.; Mülhaupt, R. *Macromolecules* **1999**, *32*, 4240.

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

(23) Hölter, D.; Burgath, A.; Frey, H. *Acta Polym.* **1997**, *48*, 30.

(24) Wojtech, B. *Makromol. Chem.* **1966**, *66*, 180.

(25) Jedlinski, Z.; Kowalczuk, M.; Kurcok, P. *J. Macromol. Sci., Pure Appl. Chem. A29* **1992**, *12*, 1223.

(26) Flory, P. J. *J. Am. Chem. Soc.* **1940**, *62*, 1561.

(27) Bayer, V.; Stadler, R.; Schmidt, M. *Polym. Prepr.* **1993**, *34* (2), 572.

(28) Naraghi, K. S.; Meneghetti, S. P.; Lutz, P. J., manuscript in preparation.

MA991192P