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Polymer 42 (2001) 4483–4491
polymer
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Synthesis and polymerization of novel oxirane bearing an aliphatic double chain moiety

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Received 22 June 2000; received in revised form 25 October 2000; accepted 8 November 2000

Dedicated to Prof. Dr I.M. Panayotov on the occasion of his 75th birthday

Abstract

A novel epoxide monomer, 1,3-didodecyloxy-2-glycidyl-glycerol (DDGG), bearing an aliphatic double chain was prepared. DDGG was anionically homopolymerized and block copolymerized with ethylene oxide (EO). The polymers were characterized by ^{1}H nuclear magnetic resonance spectroscopy, gel permeation chromatography, vapor pressure osmometry, and differential scanning calorimetry. The decrease in transmittance of the aqueous solutions of the copolymer, denoted $EO_{115}DDGG_2$, with raising temperature and/or concentration was attributed to the presence of aggregates. An anomalous increase in the transmittance at 35°C was noted as well. A dye solubilization method was used to demonstrate the ability of $EO_{115}DDGG_2$ to associate in aqueous solution. The associative interactions gave rise to a sharp increase in viscosity. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Aliphatic double chain; Anionic polymerization; Associative interactions

1. Introduction

Phospholipids and glycolipids are abundant in living organisms. They are the major component of the cell membranes that mediate a series of important cellular functions such as cell recognition, fusion, endocytosis, exocytosis, intercellular transport, lipid exchange, and osmosis [1–7]. The phospholipids and glycolipids contain a hydrophilic head group and a lipophilic moiety that consists usually of two fatty acid chains (an aliphatic double chain). The unique hydrophobic interactions between the double chains facilitate the formation of a bilayer membrane in which the double alkyl anchorage provides a better barrier than a single alkyl one.

Various derivatives of dialkyl substituted glycerols have been synthesized and their biological activity as well as surface-active and emulsifying abilities have been tested [8–24]. The lipophilic part of these compounds is responsible for their ability to mimic the naturally occurring phospholipids and glycolipids. These lipid-like compounds differ in the nature of the hydrophilic head groups, the length and the positions of the aliphatic chains in the glycerol skeleton (1,2 or 1,3), and the type of the covalent linkage (ether or ester). They are known to form a variety of self-assembled structures that include membranes, spherical, rod-like or lamellar aggregates, liposomes, and vesicles [12–24].

The surface activity of glycerol derivatives containing an aliphatic double chain and hydrophilic polyoxyethylene (PEO) or polyglycidol moieties has been employed for the formulation of pharmaceutical and cosmetic compositions [12–18]. The effectiveness of similar compounds, which vary in the length of their PEO moieties as fusogens, has been studied [25]. Drawbacks related with hampering the close contacts at the lipophilic parts, leakage of encapsulated substances from the internal water pool, and complete damage of the membrane in reconstituted liposomes have been reported. One can assume that short blocks of monomer units bearing an aliphatic double chain will provide a better anchorage of the copolymer molecule resulting in stabilization of the membrane and improvement in its barrier function. The reagents for all derivatives discussed above, however, are dialkyl substituted glycerols. These glycerols do not contain polymerizable groups, which limits the possibilities for creating amphiphilic polymers with different architectures. Consequently, the synthesis of a monomer bearing both a polymerizable group and an

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PII: S0032-3861(00)00826-0

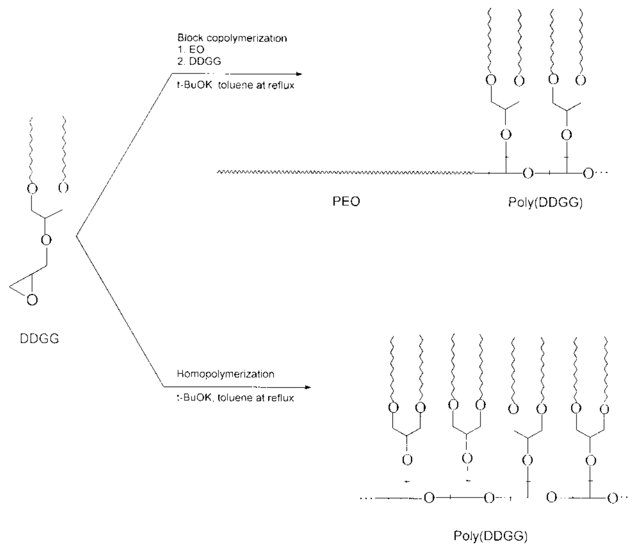

Fig. 1. Synthesis of block copolymers and homopolymers of 1,3-didodecyloxy-2-glycidyl-glycerol.

aliphatic double chain would allow the production of a new class of amphiphilic copolymers with controllable hydrophilic/hydrophobic character, hence with desired surface-active and self-assembling properties. The homopolymers and block copolymers are considered to be promising materials not only as emulsifiers, solubilizing agents, vehicles for active products but also in cellular engineering as fusogens.

The present work deals with the synthesis of a novel oxirane, 1,3-didodecyloxy-2-glycidyl-glycerol (hereinafter DDGG), and its anionic homopolymerization and block copolymerization with ethylene oxide (Fig. 1). As can be seen, the polymerizable epoxy group is linked to a residue consisting of a glycerol skeleton with two fatty chain substituents. Copolymers with ethylene oxide, containing short blocks of DDGG, are expected to possess biological activity different from that of the naturally occurring substances or the synthetic derivatives of the dialkyl substituted glycerols discussed above. On the other hand, the high hydrophobicity of DDGG sequences and its unique structure would affect the surface activity of the copolymers. A strong segregation between PEO and poly(DDGG) moieties is expected which would result in higher thickening, emulsification, aggregation, and vesicles formation abilities compared to those of conventional amphiphiles.

2. Experimental

2.1. Materials

All solvents and reagents were supplied by Fluka or Aldrich. The solvents were purified by standard methods, whereas the reagents were used as received.

2.2. Monomer synthesis

Synthesis of the intermediate, 1,3-didodecyloxy-propane-2-ol: 20 g (0.108 mol) of dry 1-dodecanol was placed in a

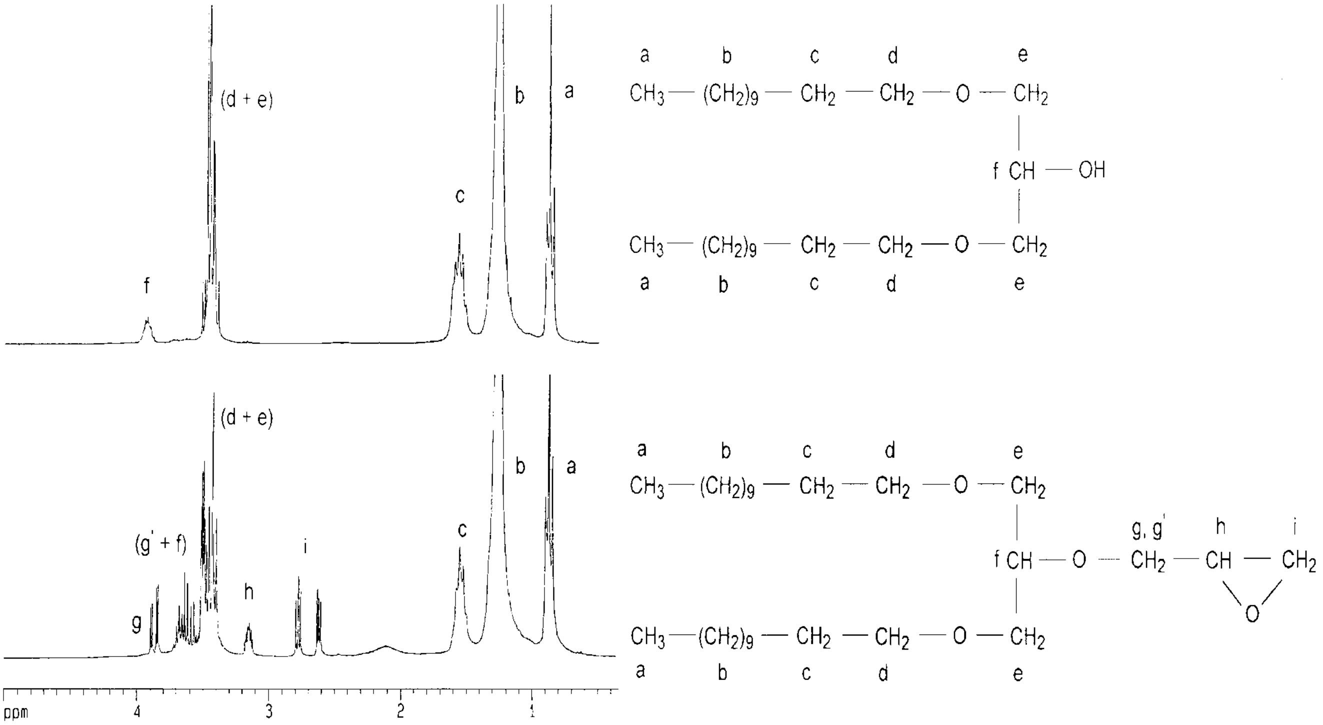

Fig. 2. ^{1}H NMR spectra of the intermediate, 1,3-didodecyloxy-propane-2-ol (top) and DDGG (bottom).

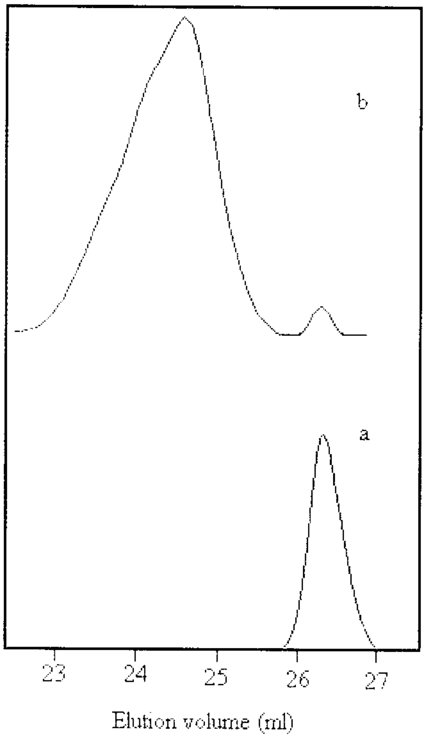

Fig. 3. Gel permeation chromatograms of samples taken before (a) and at the 25th hour after the beginning of the polymerization of DDGG in toluene (b) demonstrating the DDGG consumption.

two-necked, round-bottom flask flushed with nitrogen. 26.1 g (0.108 mol) of dodecyl glycidyl ether and 0.135 ml $SnCl_4$ were added under stirring. The stirring was maintained at 110–120°C for 24 h, then another portion of 0.135 ml of $SnCl_4$ was added and the mixture was stirred for another 70 h. The quantitative conversion of dodecyl glycidyl ether is evidenced by the lack of resonances of the epoxide protons at 2.6–3.2 ppm in the ^{1}H NMR spectrum of the product (Fig. 2, top). The product was recrystallized twice from hexane. Yield 42.1%, m.p. 40–42°C. Elemental analysis (%): C, 75.70 (found 75.56); H, 13.08 (found 13.19); O, 11.22 (found 11.37).

Synthesis of DDGG: In a nitrogen-flushed two-necked, round-bottom flask equipped with a reflux condenser 3.9 g (9.1×10^{-3} mol) of 1,3-didodecyloxy-propane-2-ol was dissolved in 50 ml of freshly distilled THF. 0.35 g (14.6×10^{-3} mol) of solid NaH was added to the solution under stirring. The mixture was heated up to 50°C and stirred for 24 h. Then 2.0 g (14.6×10^{-3} mol) of epibromohydrin was added dropwise and the reaction mixture was stirred at 50°C for another 48 h. The solid and THF were removed by centrifugation and rotary evaporation, respectively. The excess of epibromohydrin was removed under vacuum with sporadic heating up to 100°C. The purity of the product was checked by ^{1}H NMR (Fig. 2, bottom) from the relative intensities of the epoxide protons at 2.6–3.2 ppm and the methyl protons at 0.8–0.9 ppm. Yield 89.9%, m.p. 4.1°C, according to the DSC thermogram. Elemental analysis (%): C, 74.38 (found 74.22); H, 12.40 (found 12.63); O 13.22 (found 13.30).

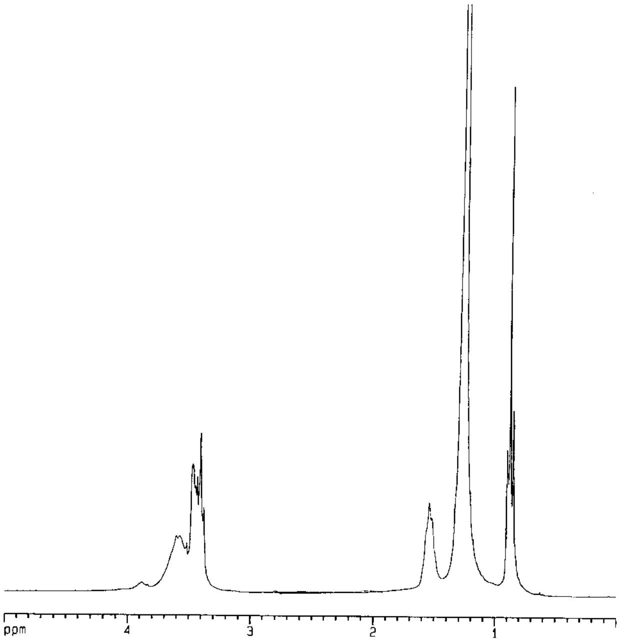

Fig. 4. ^{1}H NMR spectrum of poly(DDGG).

2.3. Polymerization

Initiator: t-BuOK, prepared according to a known procedure [26], was used as an initiator for the polymerizations.

Homopolymerization: 0.9 g (1.91×10^{-3} mol) of DDGG dissolved in 10 ml of dry toluene was placed in a 25 ml three-necked flask fitted with a nitrogen inlet, a reflux condenser outlet, and a rubber septum. 1.5 ml of a solution of *t*-BuOK in THF, containing 2.61×10^{-4} mol of *t*-BuOK was injected via a syringe. The reaction was carried out at reflux for 25 h. The mixture contained less than 10% of a residual monomer according to the GPC (Fig. 3). Toluene and the residual monomer were removed under reduced pressure and at high (10^{-5} Torr) vacuum, respectively. The ^{1}H NMR spectrum of the homopolymer showing no resonances pertaining to the oxirane ring is given in Fig. 4. Conversion 92%.

Copolymerization: 6 ml of toluene, 2 ml of ethylene oxide and 0.03 g (2.61×10^{-4} mol) of *t*-BuOK were placed in a precooled (−4°C) reactor flushed with nitrogen. The temperature was gradually increased and the mixture was stirred at 40°C for 2 h, at 50°C for 2 h and at 60°C overnight. The system was cooled and the unreacted EO was removed under reduced pressure. 2 ml from the reaction mixture was taken out and precipitated in dry diethyl ether. The PEO precursor degree of polymerization of 115 was determined from the intensities of the resonances of the methylene protons of PEO and the methyl protons of the tertiary

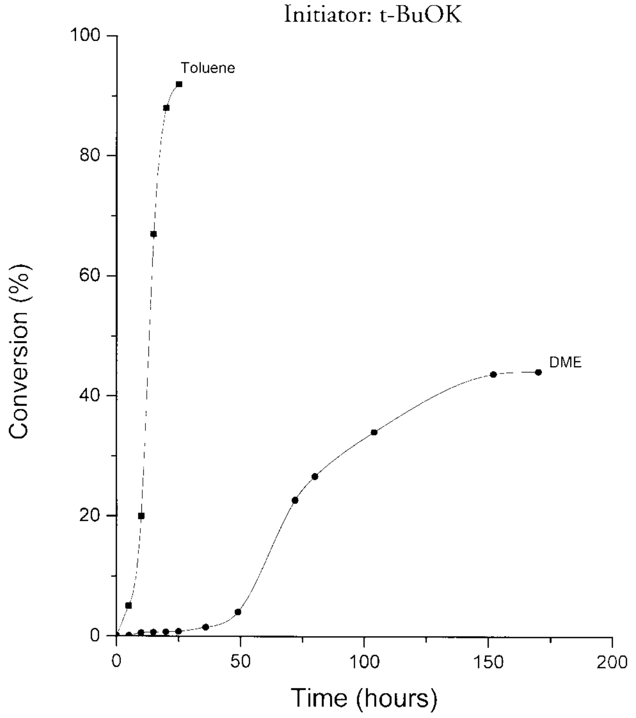

Fig. 5. Conversion of DDGG into poly(DDGG) in DME and toluene at reflux versus time.

butoxide group in the ^{1}H NMR spectrum. 0.9 g (1.91×10^{-3} mol) of DDGG dissolved in 4 ml of toluene was added and the reaction mixture was stirred at reflux for 28 h. Then toluene was removed under reduced pressure and the residue was dissolved in methylene chloride. Two fractions were isolated by precipitation in hexane and were separated: hexane-insoluble and hexane-soluble. The hexane-insoluble fraction was washed with portions of 20 ml of hexane at room temperature until no more hexane-soluble fraction was extracted. Then the product was dissolved in 10 ml of hot *n*-butanol and washed twice with 10 ml of boiling water. After evaporation of the solvent under reduced pressure 1.6 g of a white solid was isolated and dried in vacuo up to constant weight. The hexane-soluble fraction was treated similarly to yield 0.25 g of a highly viscous liquid.

2.4. Methods

Nuclear Magnetic Resonance (NMR). ^{1}H NMR spectra were recorded at 250 MHz on a Bruker 250 spectrometer. The samples were prepared as solutions in $CDCl_3$. The chemical shifts are given in ppm from tetramethylsilane. All spectra were recorded at 25°C.

Gel permeation chromatography (GPC). The GPC system (Waters) consisted of four styragel columns with nominal pore sizes of 100, 500, 500 and 1000 Å, eluted with THF at 40°C. The flow rate of the eluent was 1 ml/min. Samples were prepared as solutions in THF. Elution volumes were referenced to toluene as internal standard. Calibration was done with PEG standards and derived weight-average molar masses were determined as if samples were PEG.

Vapor pressure osmometry (VPO). The number-average molar masses were determined using a Knauer osmometer at 25°C.

Differential scanning calorimetry (DSC). DSC measurements were carried out on a Perkin–Elmer DSC-7 apparatus under an atmosphere of dry nitrogen. The first and the second heating runs as well as the cooling were conducted between −50 and 100°C at a 5°C/min scanning rate.

Solubility. A Specord UV–vis spectrometer set on transmittance at 500 nm wavelength was used to monitor the variations of the transmittance of a number of aqueous solutions of the copolymer, denoted $EO_{115}DDGG_2$, in the concentration range from 0.95×10^{-3} to 10×10^{-3} g/ml with concentration and temperature.

Viscometry. The viscosity measurements were carried out with a Ubbelohde-type viscometer equipped with a capillary of 0.45 mm diameter. The solvent (water) and solutions were filtered prior to any measurements. The apparatus was thermostated at 25°C.

Determination of critical aggregation concentration (CAC). A number of aqueous solutions of $EO_{115}DDGG_2$ in the concentration range from 0.2×10^{-3} to 10.3×10^{-3} g/ml were prepared. 25 μl of a 0.4 mM solution of 1,6-diphenyl-1,3,5-hexatriene (DPH) in methanol was added to each 2.5 ml of the copolymer solution. Solutions were incubated in dark for 16 h. The absorbance spectra in the range of $\lambda = 300–500$ nm were recorded on a Specord UV–vis spectrometer. The main absorption intensity peak, characteristic of DPH solubilized in a hydrophobic environment, was at 356 nm.

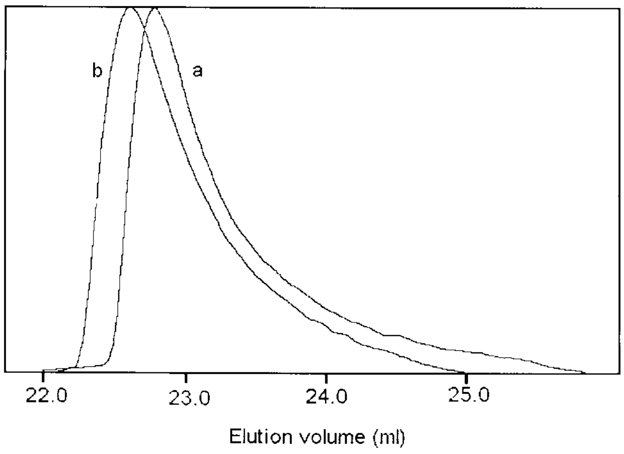

Fig. 6. GPC curves of (a) the PEO precursor and (b) the DDGG-poor fraction.

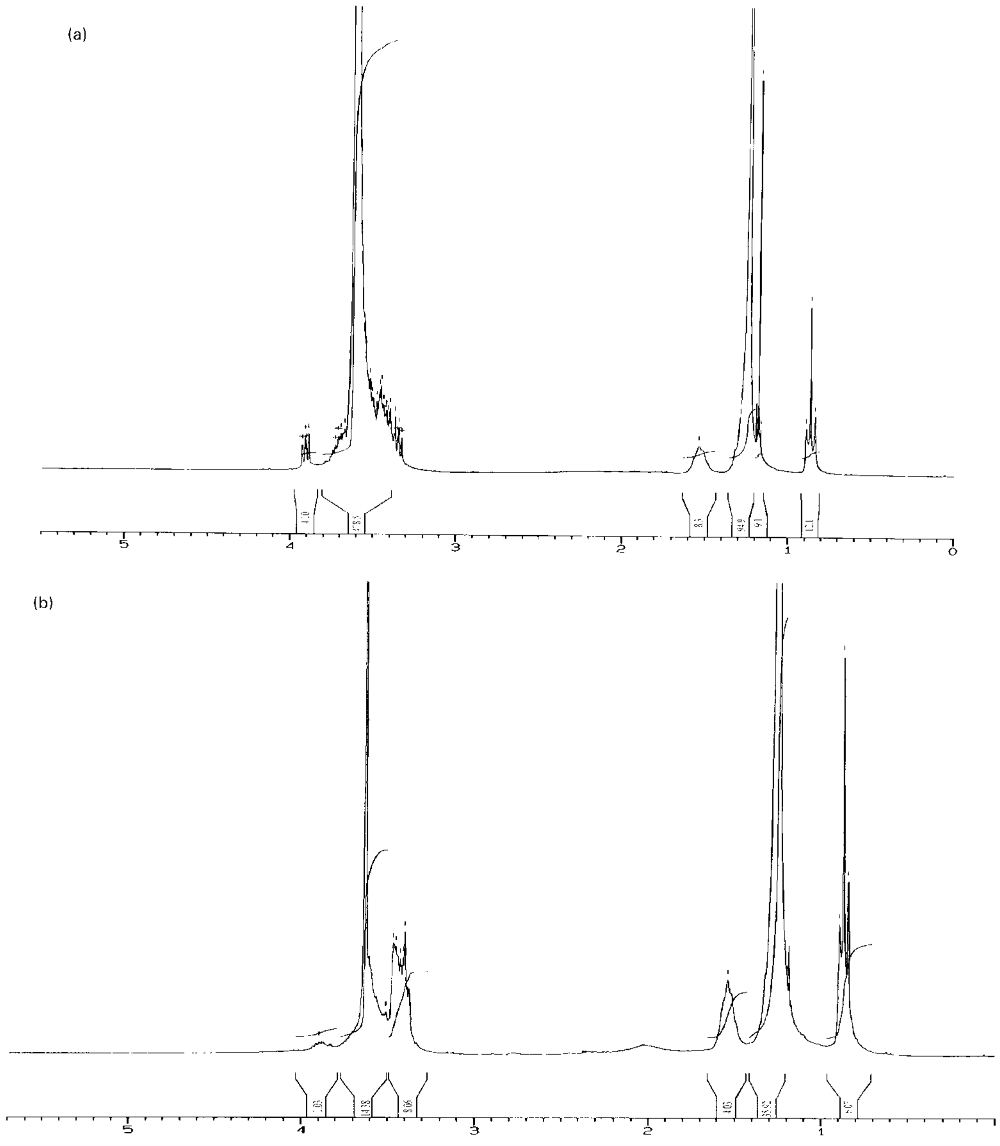

Fig. 7. ^1H NMR spectra of (a) the hexane-insoluble and (b) the hexane-soluble fractions.

3. Results and discussion

3.1. Homopolymerization

It is known that the ability of oxiranes to polymerize decreases with increasing the degree of hindrance [27]. Therefore, to achieve high conversion, the polymerization of DDGG was carried out in solvents with relatively high boiling points. The conversion of DDGG into poly(DDGG) in dimethoxyethane (DME) and toluene at reflux was monitored by GPC. This is illustrated in Fig. 3, where GPC curves of samples taken before and at the 25th hour after the beginning of the polymerization of DDGG in toluene is given. The two maxima in Fig. 3b with different intensities, assigned to the residual monomer and the polymer, poly(DDGG), are clearly separated. An average degree of polymerization of 8–9 was determined from the chromatographic data (Table 1).

S-shape trends of the conversion versus time curves for the polymerization of DDGG in both solvents were manifested (Fig. 5). The typical S-shape trends, and particularly the long induction period for the polymerization in DME, suggest a relatively complicated mechanism including an initial complex formation between the monomer and the initiator [28]. The higher rate of polymerization in toluene than that in DME was most probably due to the higher temperature of polymerization afforded in this solvent.

The homopolymer can be regarded as an amphiphilic graft copolymer with a hydrophilic polyether backbone and hydrophobic grafted aliphatic chains (see the scheme depicted in Fig. 1). On the other hand, its macromolecule

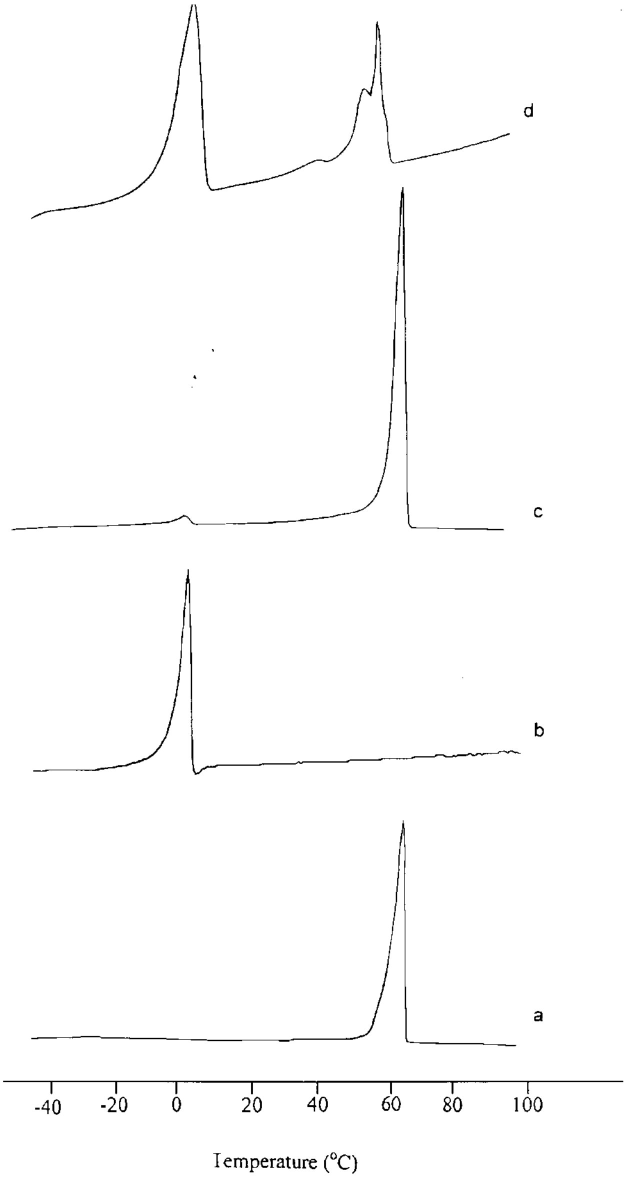

Fig. 8. DSC traces of (a) the PEO precursor, (b) poly(DDGG), (c) $EO_{115}DDGG_2$ and (d) $EO_{115}DDGG_{32}$.

resembles a monolayer of a lipid-like compound with covalently connected hydrophilic head groups. The homopolymerization of DDGG could be considered as the first stage of one of the approaches for production of polymerized supramolecular assemblies, i.e. polymerization of suitably designed amphiphilic monomers in isotropic media, followed by assembly formation [29–31]. The low degree of polymerization is advantageous, since the macromolecules of poly(DDGG) can be more easily incorporated into a supramolecular structure, e.g. a bilayer membrane, than those of a homopolymer with a high degree of polymerization [30].

3.2. Copolymerization

Two approaches for the preparation of block copolymers of DDGG with EO were attempted. In the first method, an appropriate quantity of EO was added to the living poly(DDGG) which was obtained through the polymerization of DDGG in DME with *t*-BuOK as an initiator. The GPC chromatograms and the ^1H NMR spectra of the reaction mixture, however, suggested that block copolymerization did not proceed. This might be due to either the absence of living oxyanion ends, poly(DDGG)$DDGG^-$, or to the low reactivity of the latter. As described elsewhere [32] the ethoxylation of poly(oxybutylene) oxyanion did not proceed quantitatively due to the low reactivity of the latter.

The block copolymers were successfully synthesized in toluene using the alternate approach: an appropriate quantity of DDGG was added to a solution of living PEO in toluene. After the completion of the reaction, toluene was removed and two fractions were isolated: hexane-insoluble and hexane-soluble.

The blocky structures of both fractions were unambiguously proved by GPC. The GPC curves of the PEO precursor and the hexane-insoluble fractions are given in Fig. 6. The distribution of the hexane-soluble fraction was broader (Table 1) than that of the hexane-insoluble fraction with a pronounced shoulder at the side corresponding to high molar masses. The compositions of the two fractions were determined from the relative intensities of the resonances of the methylene protons of PEO at 3.5–3.7 ppm and the methyl protons of the dodecyl chains at 0.8 ppm (Fig. 7), assuming that the degree of polymerization of the PEO precursor was 115 (see Section 2). The compositions are as follows: hexane-insoluble fraction — $EO_{115}DDGG_2$; hexane-soluble fraction — $EO_{115}DDGG_{32}$.

3.3. Properties

3.3.1. Thermal behavior

The DSC thermograms for the PEO precursor, poly(DDGG), and the two block copolymers are given in Fig. 8. The endothermic peaks correspond to the melting of

Table 1
Molar mass characteristics of the products; M_w (GPC) and M_n (VPO) of the monomer, DDGG, were 700 and 490, respectively

	M_w (g/mol) (GPC)	M_w/M_n (GPC)	M_n (g/mol) (VPO)
Poly(DDGG)	5970	1.37	-
PEO-precursor	4500	1.06	5000
Hexane-insoluble fraction	5600	1.19	6000
Hexane-soluble fraction	6400	1.57	–

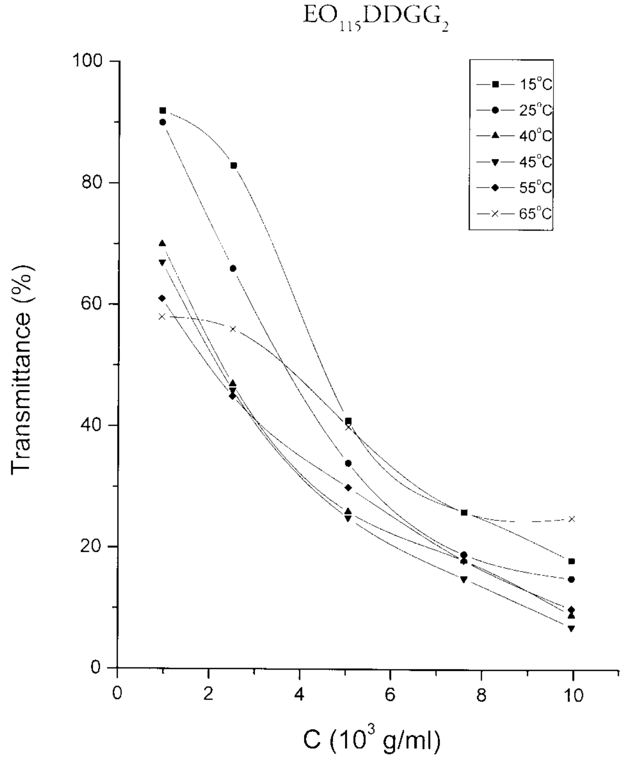

Fig. 9. Variation of the transmittance of aqueous solutions of $EO_{115}DDGG_2$ with concentration at various temperatures. Symbols are defined in the inset table.

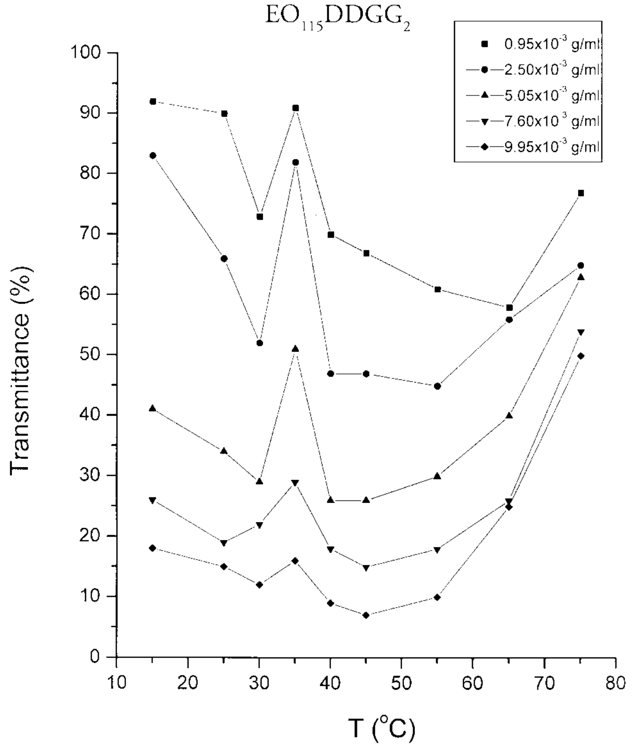

Fig. 10. Variation of the transmittance of aqueous solutions of $EO_{115}DDGG_2$ with temperature at various concentrations. Symbols are defined in the inset table.

either PEO or poly(DDGG) moieties. As seen, the melting peaks of the PEO and poly(DDGG) moieties for the block copolymers are separated, which indicates that the blocks are not miscible. This is not surprising since the two blocks have different chemical structures and could be advantageous as far as the aggregate size and the solubilization power of the copolymers in selective solvents are concerned; as noted elsewhere [33] the higher the immiscibility of the incompatible entities, the larger the aggregates and the stronger the solubilization.

3.3.2. Aqueous solution properties — solubility

Poly(DDGG) and the copolymer $EO_{115}DDGG_{32}$ were not soluble in water. The solubility in water of $EO_{115}DDGG_2$ was investigated by monitoring the variations of the transmittance (τ) with concentration (C) and temperature (t). Fig. 9 shows a number of τ/C curves at various temperatures. The increase of temperature and concentration is known to induce micellization of ethylene oxide–propylene oxide and ethylene oxide–butylene oxide block copolymers in selective solvents. On the other hand, the presence of aggregates causes an increase of the scattered light intensity. Here, the decrease in τ with raising either C or t was attributed to the increase of the scattering that originated from the appearance of aggregates.

The behavior of the aqueous solutions of $EO_{115}DDGG_2$ in the temperature range of 25–40°C deviated from the expected one. This is seen as a sharp increase of the transmittance at 35°C (Fig. 10). A similar anomalous behavior of block copolymers in selective solvents has been observed previously. It has been explained in terms of solubilization of hydrophobic domains originating from impurities [34] or phase separation of the molecular solutions [35]. In other papers the anomalous behavior has been ascribed to the changes in the aggregate shapes [36] and dimensions [37] upon a deterioration of the solvent quality. It is unlikely that $EO_{115}DDGG_2$ contained hydrophobic impurities since it was adequately purified. We consider that the former and the latter explanations, i.e. the redistribution of the aggregate size and the shape transformation, are quite plausible as far as the formation of vesicles of a various size and shape is assumed. The peculiarities of the behavior of the aqueous solutions of $EO_{115}DDGG_2$ deserve further attention and are an object of our future publication.

3.3.3. Viscosity measurements

Fig. 11 shows the variations of the reduced viscosity, η_{red}, of $EO_{115}DDGG_2$ and PEO precursor in aqueous solutions. The concentration dependence of η_{red} for the PEO precursor was linear and gave an intercept, corresponding to the limiting viscosity, of 12.6 ml/g. The equation of Mark–Houwink with $K = 2.4 \times 10^{-4}$ dl/g and $\alpha = 0.73$ [38] was used to calculate the molar mass of the PEO precursor. A value of 5300 was determined, which is consistent with the

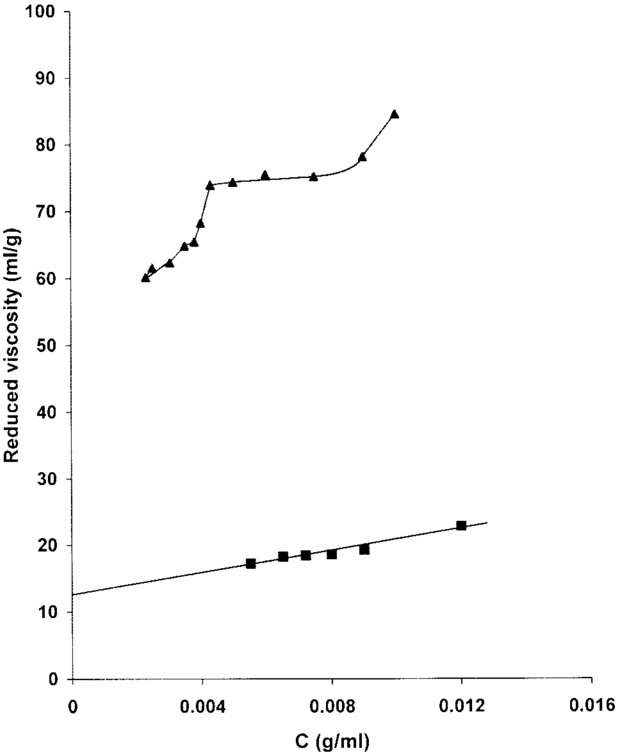

Fig. 11. Variation of the reduced viscosity of the PEO precursor (■) and $EO_{115}DDGG_2$ (▲) as a function of concentration in aqueous solutions at 25°C.

data from other analyses (Table 1). The concentration dependence of η_{red} for $EO_{115}DDGG_2$ was much more complicated. Firstly, the viscosity of the copolymer solutions was more than four times higher than that of the solutions of the PEO precursor at equal concentrations. Secondly, two pronounced breaks in the concentration dependence of η_{red} were clearly seen: one at 4×10^{-3} g/ml and a smooth change at around 1×10^{-2} g/ml. Obviously, the associative interactions of the block copolymer chains affected the reduced viscosity; the low concentration break could be associated with the critical aggregation concentration, whereas the smooth change at the high concentration range could be due to clustering of the aggregates.

3.3.4. Solubilization of hydrophobic substances and CAC determination

The solubilization aptitude of $EO_{115}DDGG_2$ was probed by studying the behavior of DPH in the copolymer aqueous solutions. DPH is a well-known probe of membrane interiors. It has been employed to study the fluidity of membranes [39,40] and to measure dynamic phenomena in vesicles [41,42]. DPH solubilization has been used previously for the determination of the critical micellization concentrations of various detergents [43–45]. A typical plot of DPH absorbance at 356 nm versus $EO_{115}DDGG_2$ concentration is presented in Fig. 12. The CAC value in the vicinity of 2×10^{-3} g/ml determined by this technique was in agreement with the first break in η_{red} versus C plot in Fig. 11.

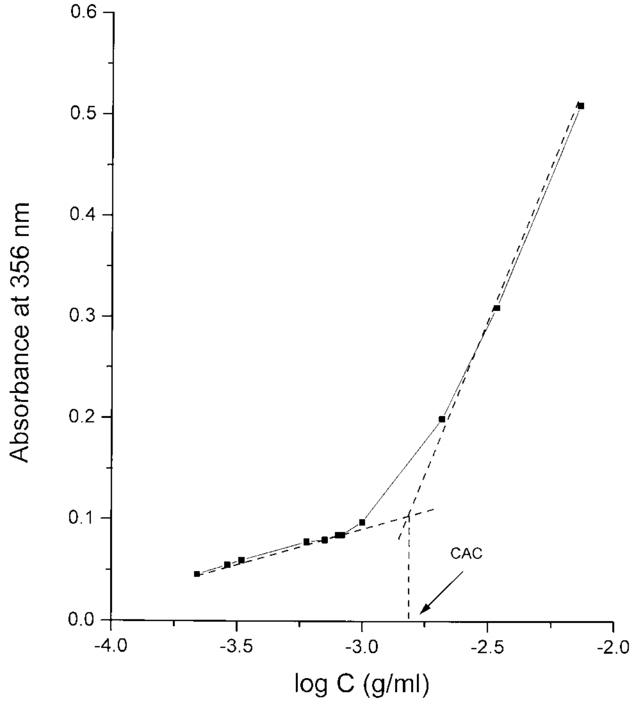

Fig. 12. Variation of the absorbance of DPH at 356 nm as a function of $EO_{115}DDGG_2$ concentration in aqueous solutions.

4. Concluding remarks

In this paper we reported the synthesis and polymerization of a novel epoxide monomer, bearing an aliphatic double chain — 1,3-didodecyloxy-2-glycidyl-glycerol (DDGG). We have shown that DDGG was able to polymerize, and a novel and original homopolymer as well as block copolymers with EO were synthesized and their properties studied.

Poly(DDGG) with degree of polymerization 8–9 and conversion of more than 90% was obtained using *t*-BuOK as an initiator in toluene at reflux. It was found that the rate of polymerization and the conversion of DDGG into poly(DDGG) were much lower when the polymerization was carried out in DME.

Block copolymers were prepared by sequential anionic polymerization of EO followed by DDGG. DSC thermograms showed that the melting peaks of PEO and poly(DDGG) moieties were separated, suggesting a clear segregation between blocks. The decrease of the transmittance of the aqueous solutions of the copolymer, $EO_{115}DDGG_2$, with raising temperature and/or concentration was attributed to the appearance of aggregates. An anomalous increase in the transmittance at 35°C was noted as well. The reduced viscosity of $EO_{115}DDGG_2$ was more than four times that of the PEO precursor, indicating associative interactions of DDGG sequences in aqueous solutions. The associative interactions were confirmed by using a dye solubilization method.

A natural extension of this work will be to synthesize, characterize, and to present preliminary investigations of triblock copolymers of EO and DDGG of both ABA and BAB types. Obviously, more fundamental studies using powerful techniques are needed for a better understanding of the behavior of these original and promising polymer materials.

Acknowledgements

Financial support from the National Fund "Scientific Research" (project X-808) is gratefully acknowledged. The authors thank Dr A. Thies, Union Carbide Corporation, Bound Brook, NJ, for helpful discussions.

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