Polymer Bulletin 40, 461–468 (1998)

Polymer Bulletin

Poly(α-*t*-butoxy-ω-styrylo-glycidol): a new reactive surfactant.

Andrzej Dworak[1,*], Ivan Panchev[2], Barbara Trzebicka[1], Wojciech Walach[1]

[1] Institute of Coal Chemistry, Polish Academy of Sciences, ul. Sowi ńskiego 5, PL-44-102 Gliwice, Poland
[2] Institute of Polymers, Bulgarian Academy of Sciences, Sofia, Bulgaria

Received: 13 January 1998/Revised version: 24 February 1998/Accepted: 5 March 1998

Summary

Poly(α-t-butoxy-ω-styrylo-ethoxy ethyl glycidyl ether) was synthesized via the termination of the potassium t-butoxide initiated anionic polymerization of ethoxy ethyl glycidyl ether with p-chloromethylstyrene. The macromonomer was copolymerized with styrene. Subsequent hydrolysis of the copolymers leads to polystyrene - graft - polyglycidol. Poly(α-t-butoxy-ω-styrylo-glycidol), synthesized through the hydrolysis of the macromonomer so obtained, acts as reactive emulsifier (surfmer) in the emulsion copolymerization of styrene in water.

Introduction

Macromonomers containing a polymerizable, in most cases hydrophobic group and a hydrophilic extender chain are of growing interest as reactive emulsifiers (surfmers) in the emulsion and dispersion polymerization (for reviews, see (1, 2)). The hydrophilic chain stabilizes micelles. The hydrophobic group, in most cases containing a reactive double bond, is incorporated into a polymer chain in the course of a radical polymerization. Several such macromonomers have been described, most of them containing a styryl (3, 4) or acryl (5, 6, 7, 8) reactive group and a hydrophilic, ionic (9, 10) or non ionic (11) side chain. Conditions for their application have been optimized (12). No macromonomers of this kind have been reported which contain a large amount of non ionic functional groups in the hydrophilic chain.

This work reports the synthesis and polymerizability of poly(α-t-butoxy-ω)-stvrylo-glycidol), a macromonomer of well defined structure which combines a polymerizable styrene group with a strongly hydrophilic polyether chain containing a hydroxyl group in each repeat unit.

Experimental

Ethoxy ethyl glycidyl ether was synthesized from glycidol and ethyl vinyl ether according to (13) and distilled prior to use. A fraction of purity > 99.8% (GC) was used.

THF was refluxed over Na/K alloy.

Styrene and p-chloromethyl styrene were distilled.

Potassium t-butoxide (Aldrich) was used as received.

* Corresponding author

Synthesis of the macromonomer: The initiator was placed under dry nitrogen in a dry reactor. Dry THF (10 ml) was added, the reactor was cooled to -50°C and ethoxy ethyl glycidyl ether (10 ml) was added. The polymerization was carried out at 60° for 17 h. Its progress was checked by gas chromatography. p-Chloromethyl styrene (1.2 times the molar amount of the initiator) was added and the mixture left for 2 h. The solvent was evaporated at 30°C, the polymer dissolved in benzene and centrifuged to remove the precipitated potassium chloride. The polymer was dried under reduced pressure.

Copolymerization of the macromonomer with styrene in benzene solution: The necessary amount of the macromonomer, styrene (1.5 ml) and AIBN (0.05 g) were dissolved in benzene (5 ml). The mixture was degassed by several freeze - thaw cycles under high vacuum and polymerized for 6 h at 60°C. The polymer was precipitated in n-heptane and dried.

Hydrolysis: The polymer (1g) was dissolved in formic acid (10 ml). After 20 min most of the formic acid was evaporated under reduced pressure at room temperature, the remainder dissolved in a mixture of 1,2-dioxane (12 ml) and methanol (7 ml) and made alkaline with 2N KOH until pH > 12. After 24 h the solvents were evaporated, the polymer dissolved in water and the solution desalinated using ion exchange columns. Water was evaporated and the polymer dried at 30°C.

Emulsion copolymerization of the macromonomer with styrene: The necessary amount of the macromonomer was dissolved under N_2 in water/methanol mixture (7 : 3) and styrene (5.5 ml) was added. The mixture was purged with nitrogen and degassed for 15 min in an ultrasonic bath. $Na_2S_2O_8$ (2 mol%) was added and the reactor placed for 48 h at 60°C under intense stirring. The polymer was centrifuged, washed with methanol and dried under reduced pressure.

GPC analyses were carried out in THF using 2 x Plgel MIXED C and a PL 100 columns. Polystyrene calibration was applied.

^{1}H NMR spectra were measured at 300 MHz in $CDCl_3$ or DMSO.

Results and discussion

Synthesis of the macromonomer

The polymerization of glycidol, 2,3-epoxypropanol-1, both cationic and anionic, is known to yield highly branched oligomers (14, 15). The structure of obtained polymers is difficult to control. In order to obtain linear, well defined polymers the hydroxyl group has to be protected. Vandenberg described the polymerization of trimethyl silyl glycidyl ether (14). Spassky protected the hydroxyl group through its reaction with ethyl vinyl ether and showed that the ethoxy ethyl glycidyl ether obtained may be polymerized under the action of anionic initiators (16). He further described the way to remove the protecting group without degrading the polyether chain, which is otherwise prone to destruction in acid media. The initiators used (graphite/potassium, SALCEN, CsOH) required that the reaction was carried out in heterogeneous systems, which made the control of the molecular weight difficult and resulted in rather broad molecular weight distribution.

In order to synthesize the desired macromonomer via the termination method it was necessary to carry out the polymerization in a homogenous system under conditions close to living. We established that the polymerization of ethoxy ethyl glycidyl ether initiated with potassium t-butoxide in THF fulfills these conditions. Within a wide range the degree of polymerization corresponds well to the initial monomer to initiator ratio (table 1). The monomer consumption under the chosen condition was almost complete, as indicated by gas chromatography. The polymerization may easily be terminated by methyl iodide, the methyl group of the terminating agent being incorporated into the polymer chain, which was proved by the ^{1}H NMR spectroscopy of the polymers of lower molecular weight.

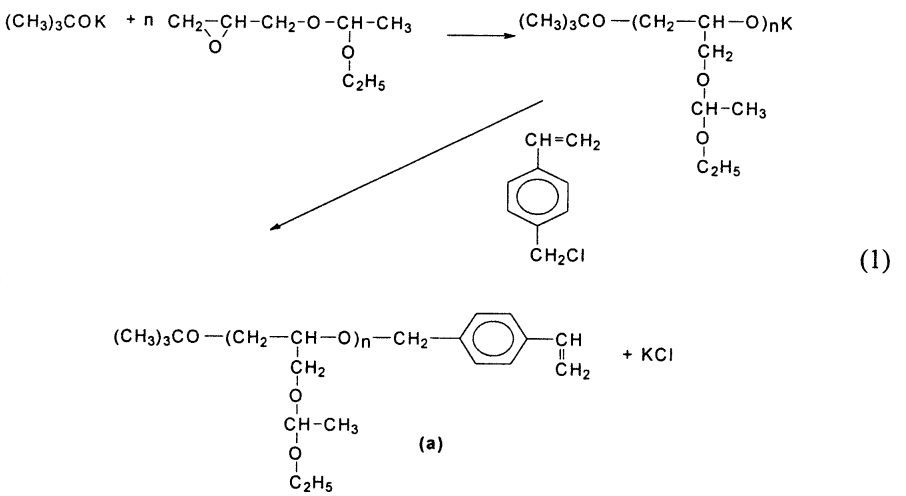
Table 1. Polymerization of ethoxy ethyl glycidyl ether initiated with potassium t-butoxide in THF ([M]$_o$ = 3.4 mol/L, 60°C)

M_n calculated from feed	M_n *) (GPC)	M_w *) (GPC)	M_w/M_n *)
3 000	2550	3040	1.19
5 000	6400	7630	1.20
10 000	8900	10480	1.18
20 000	13390	15850	1.18

*) *Determined using polystyrene standards.*

This opens the following route of the synthesis of styryl terminated polyglycidol macromonomer.

The polymerization of ethoxy ethyl glycidyl ether is initiated with pottasium t-butoxide and terminated with p-chloromethyl styrene:



The reaction leads to styrene terminated polymers **(a)** of ethoxy ethyl glycidyl ether of rather narrow molecular weight distribution. The ^{1}H NMR spectra (fig.1) indicated that the chains contained styryl groups. The quantitative analysis of the spectra and the molecular weights measured by GPC confirm that the termination is almost complete (table 2).

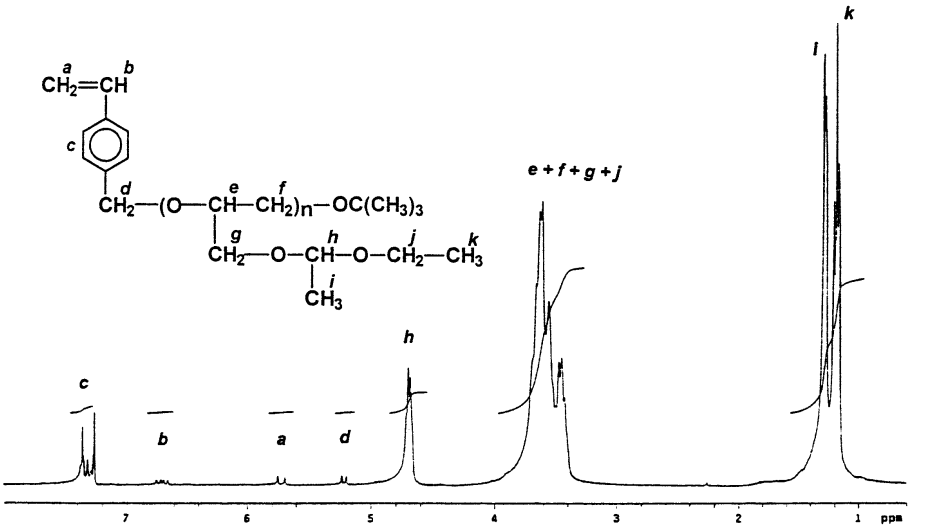
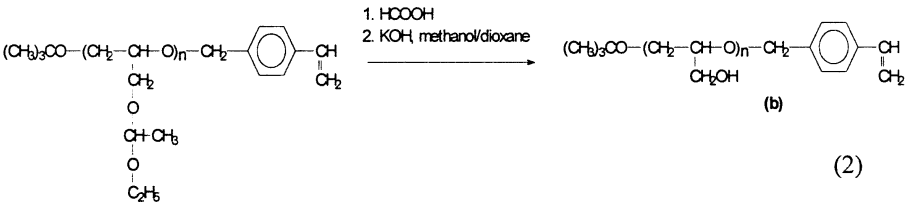


Fig. 1. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of polymer **(a)**.

Table 2. Styrene terminated polyglycidol macromonomers

No.	$[M]_o/[I]_o$	M_n			M_w/M_n
		calc. from feed	determined by ^{1}H NMR	determined by GPC	
1	14	2430	2500	2800	1.25
2	21	3550	3100	3400	1.26
3	27	4510	5000	5200	1.22

The protecting group may be removed in the way described by Spassky (16):



(2)

yielding styrene terminated polyglycidol chains, as confirmed by ^{1}H NMR (fig. 2). This way of the hydrolysis via the formic acid esters minimizes the degradation of the polyether chains.

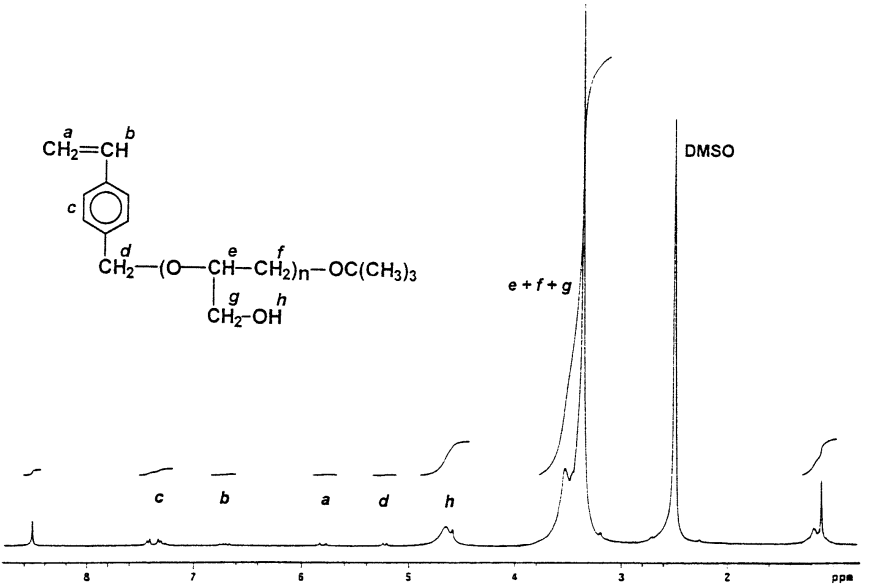
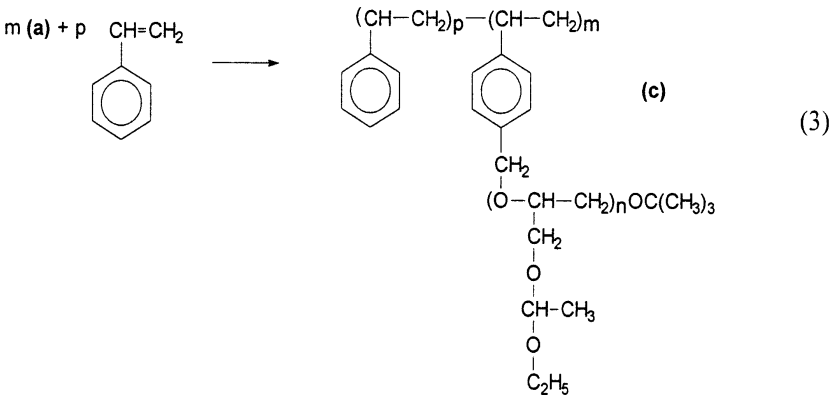


Fig. 2. ^{1}H NMR spectrum (DMSO, 300 MHz) of poly(α-t-butoxy-ω-styrylo-glycidol) **(b)**

Like all polymers of glycidol, the hydrolyzed macromonomers are soluble in water, lower alcohols, DMSO and DMF, but insoluble in most common organic solvents.

Copolymerization of the macromonomer (a) with styrene

To check the polymerizability of the styrene double bond in the macromonomers we carried out the radical copolymerization of the poly(α-t-butoxy-ω-styrylo ethoxy ethyl glycidyl ether) with styrene in benzene solution:



(3)

GPC analysis indicates that the copolymerization takes place and the ^{1}H NMR spectra allow the determination of the composition of the copolymers (c) obtained (fig. 3, table 3).

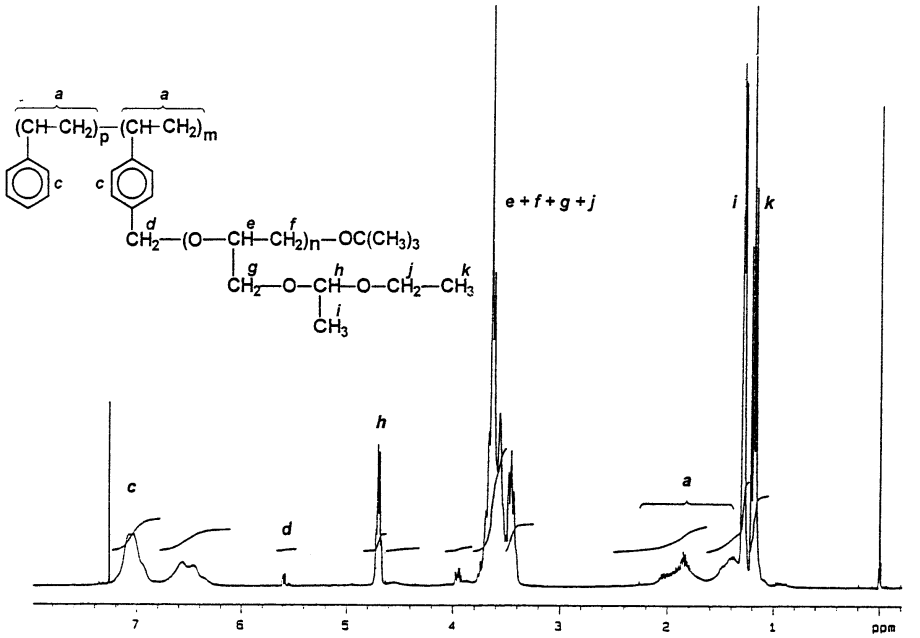


Fig. 3. ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of the copolymer of poly(α-t-butoxy-ω-styrylo-ethoxy ethyl glycidyl ether) with styrene **(c)**.

Table 3. Copolymerization of poly(α-t-butoxy-ω-styrylo-ethoxy ethyl glycidyl ether) with styrene

Macromonomer		Copolymer			
No.*)	Weight-% in feed	Yield [%]	Conversion of the macro-monomer [%]	M_n	M_w/M_n
1	77	70	62	59000	1.66
1	27	65	55	35000	2.28
2	70	75	55	71000	2.31
2	31	70	65	52000	2.45

*) see table 2

The data in table 3 show that the macromonomer undergoes the copolymerization with styrene. Copolymers containing over 50% polyether structural units are obtained. In no case was total conversion of the macromonomer achieved.

The protective acetal groups of the copolymer may be removed as described in eq. (2). leading to polystyrene-graft-polyglycidol. The amphiphilic character of these graft co-polymers, which contain hydrophobic polystyrene main chain and hydrophilic polyglyci-dol side units, limits their solubility to strongly polar solvents, like DMSO or (less) DMF.

Emulsion copolymerization of poly(α-t-butoxy-ω-styrylo-glycidol) (b) with styrene

The amphiphilic character of the water soluble poly(α-t-butoxy-ω-stirylo-glycidol), which contains the hydrophilic polyglycidol chain and the hydrophobic styrene group suggests its application as a reactive surfactant in emulsion copolymerization with styrene.

The addition of 0.6 weight-% to 10 weight-0/6-of the macromonomer to the system allows a stable emulsion of styrene in water to be obtained without addition of an external emulsifier. The results of the experiments are shown in table 4.

Table 4. Emulsion copolymerization of poly(α-t-butoxy-ω-styrylo-glycidol) with styrene

Macromonomer		Copolymer			
No.*)	Concentration [weight-%]	Yield [%]	M_n	M_w/M_n	Conversion of the macro-monomer [%]
1	10	89	730000	3.8	62
1	5	70	810000	3.6	75
1	1	80	590000	4.1	80
1	0.6	65	720000	3.7	n.d.
2	5	80	810000	3.7	81
2	1	75	645000	3.7	85
2	0.6	60	740000	4.1	n.d.

*) see table 2

The polymerization initiated with sodium peroxy disulfate leads to copolymers. GPC measurements indicate high molecular weight and rather broad monomodal distribution. However, it should be noticed that the copolymers obtained contain polyglycidol side chains and may associate in THF, which is a non solvent for polyglycidol. This may lead to incorrect GPC data. In the ^{1}H NMR spectra the signals of the protons of polyglycidol structural units may be observed, but their intensity is too low for quantitative determination. To measure the amount of the macromonomer incorporated into the copolymer the amount of the hydroxyl groups in the copolymer was determined by titration according to ASTM 2880. The results indicate that in each experiment the macromonomer was incorporated into the copolymer, but in no case was its conversion complete.

The optimization of the conditions for the application of this macromonomer as a reactive surfactant and the choice of the condition necessary to obtain the copolymer as nanoparticles of well defined size, enriched with the hydroxyl groups on their surface, will be the subject of a separate report.

References

1. Nagai K (1996) TRIP 4:122
2. Ito K (1997) Macromonomers. In: Salamone JW (ed) Encyclopedia of polymeric materials. CRC Press, Roca Baton, p. 3927
3. Tsaur S-R, Fitch RM (1987) J. Colloid Interface Sci. 115:450
4. Ottewil RH, Satgurunathan R (1987) Coll. Polym. Sci. 265:845
5. Uyama H, Honda Y, Kobayashi S (1993) J. Polym. Sci. Part A: Polym. Chem. 31:123
6. Akashi M, Chao D, Yashima E, Miyauchi N (1990) J. Appl. Polym. Sci. 39:2027
7. Ito K, Yokoyama S, Arakawa F (1986) Polym. Bull. 16:345
8. Prestige C, Tadros TF (1988) J. Coll. Interf. Sci. 124:660
9. Yeoh KW, Chew CH, Gan LM, Kohl LL (1989) Polym. Bull. 22:123
10. Yeoh KW, Chew CH, Gan LM, Kohl LL (1990) J. Macromol. Sci.-Chem. A27:63
11. Nagai K, Elias H-G (1987) Makromol. Chem. 188:1095
12. Schoonbrood HAS, Asua JM (1997) Macromolecules 30:6034
13. Fitton A, Hill J, Jane D, Miller R (1987) Synthesis 1140
14. Vandenberg EJ (1985) J. Polym. Sci. Polym. Chem. 23:915
15. Dworak A, Walach W, Trzebicka B (1995) Macromol. Chem. Phys. 196:1963
16. Taton D, Le Borgne A, Sepulchre M, Spassky N (1994) Macromol. Chem. Phys. 195:139