Polymer Bulletin 7, 17-22 (1982)

Polymer Bulletin

Synthesis of Polyethylene Oxide Macromers

Patrick Masson, Gérard Beinert, Emile Franta and Paul Rempp

Centre de Recherches sur les Macromolécules (CNRS), 6, rue Boussingault,
F-67083 Strasbourg Cedex, France

SUMMARY

Anionic "living" polymerization of oxirane was shown to be efficient for the synthesis of polyethylene oxide macromers. The double bond at chain-end was introduced either upon initiation or upon deactivation. The macromers obtained were characterized carefully to establish quantitatively the presence of the end-standing double bond. The species are well defined and of narrow molecular weight distribution.

INTRODUCTION

Macromolecular monomers, currently called "macromers", are short polymer chains fitted at one chain end with a polymerizable unsaturation. Ionic polymerization methods are well suited for the synthesis of such species. A recent paper (1) was devoted to the synthesis of polyoxybutylene macromers by means of an appropriate unsaturated cationic initiator. These compounds were submitted to a detailed characterization, that demonstrated the efficiency of the method.

Polyoxyethylene macromers are even more interesting, as intermediates for the synthesis of amphiphilic graft copolymers: Polyethylene oxide is a non-ionic hydrophilic polymer.

Oxirane (ethylene oxide) is known to polymerize anionically (2) in aprotic solvents, to "living" polymers fitted at chain end with alcoholate functions. Various compounds can be used to initiate oxirane polymerization, such as cumylpotassium, diphenylmethylpotassium, potassium alcoxides. Potassium counterions provide for acceptable polymerization rates at temperatures just above ambient. Transfer and termination reactions can be avoided by choosing adequate experimental conditions: aprotic solvent (THF), inert atmosphere, no moisture in the reactor or reagents. Under these conditions the average degree of polymerization is determined by the ratio of the mole amount monomer consumed to the mole amount initiator used. The molecular weight distribution is narrow.

The synthesis of polyethylene oxide macromers by means of anionic polymerization can be attempted in two ways:

. either by using an unsaturated initiator, provided it reacts by addition onto the monomer, without side reactions involving the double bond.

. or by reacting the active sites of the "living" polymer

0170-0839/82/0007/0017/$01.20

with an unsaturated electrophile.

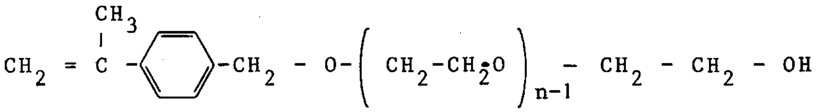
Both pathways have been applied. In this paper the results obtained are presented and discussed.

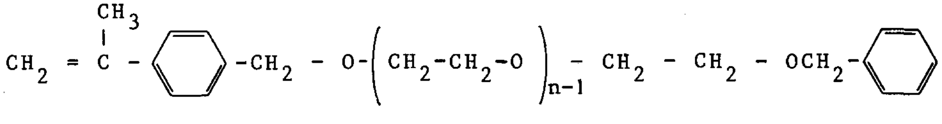
I - POLYMERIZATION OF OXIRANE BY MEANS OF AN UNSATURATED INITIATOR

We wanted the initiator to contain an activated double bond, to be relatively easy to prepare and to react readily by addition onto oxirane. We chose potassium p-isopropenylbenzyl alcoholate which fulfills these conditions. Side reactions affecting the double bond are prevented: because of its relatively low nucleophilicity the alcoxide does not react with α-methylstyrene type double bonds.

The alcoholate is made in situ from the corresponding alcohol, diphenylmethyl-K being the metalating agent. This compound does not attack the double bond under the conditions used. The alcoholate is insoluble, owing to associations between alcoxide functions. Thus initiation is heterogeneous. But as soon as the average degree of polymerization of the growing chains is of the order of 5 the reaction mixture becomes homogeneous. Once the polymerization has proceeded to completion, the end-standing alcoxide functions are deactivated, either protonically, or by means of benzyl chloride.

The macromers obtained should thus exhibit the structures below:





CHARACTERIZATION OF THE MACROMERS

An accurate characterization of the samples obtained is necessary to establish whether the above method is suitable. Several techniques were used:

. By means of a GPC apparatus fitted with refractometric and UV detections it was established that the samples contain α-methylstyrene type end groups, exhibiting an absorption at 250 nm (Fig.1). In addition, the $\bar{M}_w/\bar{M}_n$ ratios were found in the range 1.1 to 1.2.

. Proton NMR was used to evaluate the relative amounts of aromatic protons (at 7 ppm), of the methylene protons of the isopropenyl group (at 4.9 and 5.2 ppm), both arising from the initiator, and of the oxyethylene protons of the chain (at 3.5 ppm). Using the integral curve (Fig.2) it is possible to calculate roughly the number average molecular weight of the sample.

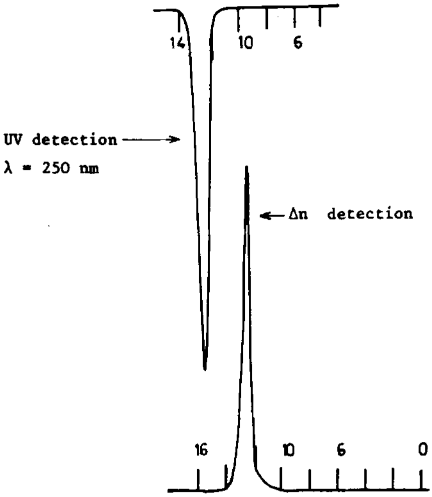


Fig. 1 - GPC diagram of sample A 2

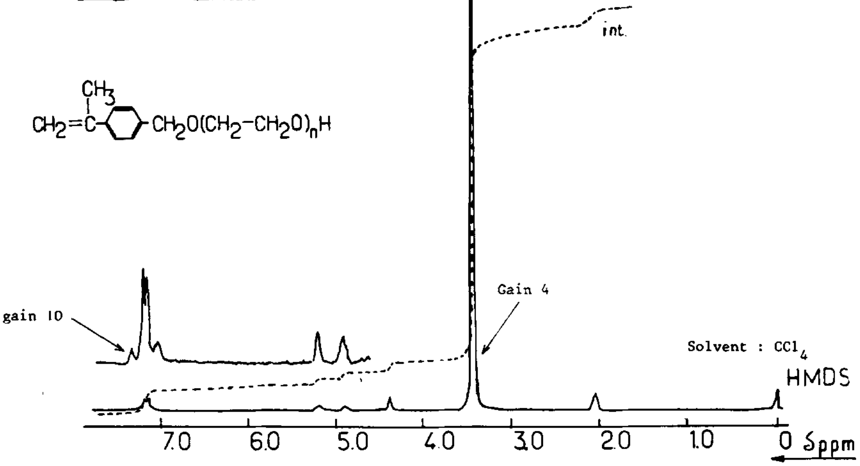


Fig. 2 - ^{1}H-NMR spectrum of sample A 4

. UV spectroscopy was also used to determine $\bar{M}_n$, assuming one α-methylstyrene type chromophore per molecule. A model compound, made specially: p.isopropenylbenzyl ethylether was used to determine the absorptivity of the chromophore. ε was found to be 12 700 $l.mol^{-1}.cm^{-1}$, at λ_{max} = 250 nm, in THF solution. From the optical density measured on each of our samples, the $\bar{M}_n$ values can be calculated easily.

. Double bond titration permits to determine the number average molecular weights of our samples, as well.

. Vapor pressure osmometry and light scattering were used to measure number- and weight averages of the molecular weights, respectively. No hypothesis is involved concerning the molecular structure of the samples investigated.

The results obtained are gathered on table 1, together with the values of $\bar{M}_n$ calculated from the monomer to initiator mole ratio. The agreement between all these values for any given sample is quite satisfactory. However the accuracy of the $\bar{M}_n$ measurements decreases as the chain length increases.

TABLE 1

Data on PEO macromers obtained with the unsaturated initiator

Ref.	Deactivating agent	Yield (%)	$\bar{M}_{n,th}$	$\bar{M}_n$ >=<	$\bar{M}_{n,NMR}$	$\bar{M}_{n,UV}$	$\bar{M}_{w,LS}$	$\bar{M}_{n,VPO}$
A 1	MeOH,H^+	75	2000	1850	1700	2000	2100	-
A 2	"	78	1800	1700	1700	2000	1800	-
A 3	"	79	4500	5200	4700	4200	4500	-
A 4	"	72	1000	1080	900	1020	-	1000
A 5	"	73	1500	1360	1300	1560	-	1310
A 6	$ClCH_2\phi$	73	1500	1460	1300	1560.)	-	1310.)
A 7	"	76	1800	1730	1600	1700.)	1900	-

.) determined on a sample deactivated protonically

We can thus state that polyoxyethylene macromers can be synthesized efficiently by means of the unsaturated initiator that was chosen. An adequate control of the molecular weights is possible. It should be stressed that in spite of the slow, heterogeneous initiation the samples exhibit narrow molecular weight distributions.

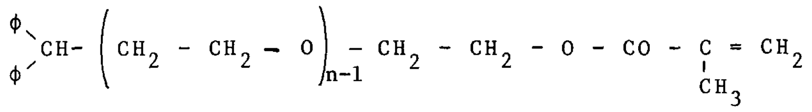
II-SYNTHESIS OF POLYOXYETHYLENE MACROMERS BY DEACTIVATION WITH AN UNSATURATED ELECTROPHILE

The alternate way we have attempted to synthesize PEO macromers involves deactivation of the alcoxide function of a monofunctional"living" PEO by means of an unsaturated electrophile. Under the experimental conditions chosen an alcoxide is unable to attack methacrylic double bonds. We have thus selected methacrylic chloride as deactivator.

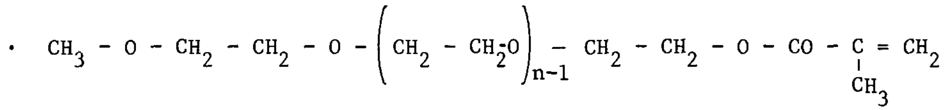
An efficient monofunctional initiator is needed to keep control of the molecular weight of the PEO chains. Two such initiators have been used: diphenylmethylpotassium and the potassium alcoxide of methoxyethanol. The advantages of the former include solubility, efficiency, and the possibility offered to determine quantitatively the endstanding diphenylmethyl groups by ^{1}H-NMR, and by UV-spectroscopy. Its drawback is that PEO chains carry a bulky hydrophobic end-group.

K-Methoxyethanolate is insoluble, and initiation is heterogeneous. Nevertheless its efficieny is satisfactory, and the PEO chains do not carry a hydrophobic group at chain end. When this initiator was used, part of the "living" PEO was sampled out and deactivated with diphenylchloromethane for purpose of characterization by NMR and UV-spectroscopy.

The PEO macromers should exhibit the structures shown below:



$$\phi_2CH-(CH_2-CH_2-O)_{n-1}-CH_2-CH_2-O-CO-\underset{CH_3}{\underset{|}{C}}=CH_2$$

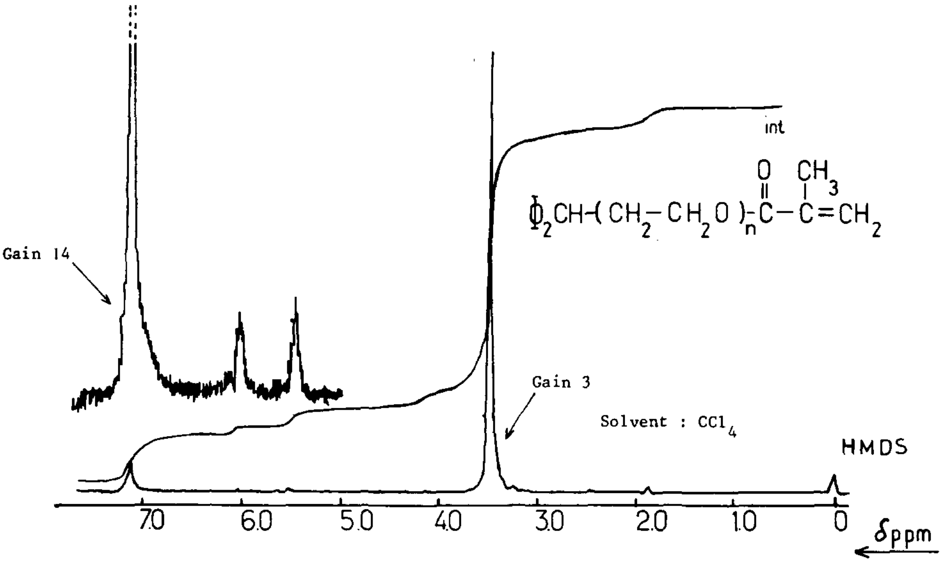


$$CH_3-O-CH_2-CH_2-O-(CH_2-CH_2-O)_{n-1}-CH_2-CH_2-O-CO-\underset{CH_3}{\underset{|}{C}}=CH_2$$

The characterization of the macromers obtained by anionic deactivation involves the same techniques as above:

- Proton NMR allows to calculate approximately the $\bar{M}_n$ values from the ratio of aromatic protons (7.0 ppm) of the end-group to the oxyethylene protons (3.5 ppm) of the chain (Fig.3)

Fig. 3 - ^{1}H-NMR spectrum of sample B 1



- UV-spectroscopy was used to determine the molecular weights, from the absorption at λ_{max} = 262 nm of the diphenylmethyl end-group in THF. If it originates from the initiator the absorptivity ε - measured on 1.1-diphenylpentane - amounts to 860 $l.mol^{-1}.cm^{-1}$. If the diphenylmethyl group results of deactivation by diphenylchloromethane, the absorptivity ε - measured on diphenylmethylbutylether - amounts to 535 $l.mol^{-1}.cm^{-1}$.

- IR-spectroscopy is well suited to detect the methacrylic ester functions: the ester carbonyl absorption located at 1730 cm^{-1} follows Beer-Lambert's law and exhibits an absorptivity coefficient of 700 $l.mol^{-1}.cm^{-1}$ in CCl_4 (from BuMA).

. Double bond titrations were performed on the macromers.

. GPC and light scattering were used, as above.

The results are gathered on table 2. The values of $\bar{M}_n$ obtained from the methods quoted are in good agreement. It can be concluded that the samples exhibit the structure expected; the methacrylic ester function at chain end is present, indicating that the linking reaction is close to quantitative though it is rather slow. Here again the molecular weight distributions are relatively narrow, even when the K-alcoholate is used as initiator.

TABLE 2

Data on PEO macromers obtained with the unsaturated electrophile

Ref.	Initiator	Yield (%)	$\bar{M}_{n,th}$	$\bar{M}_n$ $\asymp$	$\bar{M}_{n,NMR}$	$\bar{M}_{n,UV}$	$\bar{M}_{n,IR}$	$\bar{M}_{w,LS}$
B 1	ϕ_2CH-K	74	2000	2300	1600	1800	2400	3200
B 2	"	47	2000	1800	1400	1950	2600	2900
B 3	"	78	2000	2000	1800	1800	2000	2300
B 4	CH$_3$O-CH$_2$-CH$_2$O-K	84	4500	4600	4000 .)	3600 .)	-	5300
B 5	"	74	3600	3800	3600 .)	4200 .)	4200	4200
B 6	"	79	2000	2100	1900 .)	2000 .)	2100	2200

.) see text

CONCLUSION

Polyoxyethylene macromers can be obtained anionically in two ways, with good yields: Either an unsaturated initator is used to start the ethylene oxide polymerization; or, the "living" sites of a monofunctional PEO are reacted with an unsaturated electrophile. In both cases, the characterization of the samples has brought conclusive evidence of the success of the method.

Application of theses macromers to the synthesis of amphiphilic graft copolymers will be described in another paper. This new access to emulsion forming species is of great interest.

References

1) J. SIERRA VARGAS, J.G. ZILLIOX, P. REMPP, E. FRANTA
Polym.Bull. 3, 83 (1980)
2) F. CANDAU, F. AFSHAR-TAROMI, G. FRIEDMANN, P.REMPP
C.R.Acad.Sci. C-284, 837 (1977).

The authors are greatly indebted to Mr.E.SCHUSTER and F.ISEL for technical assistance.

Received and accepted March 5, 1982
C