

BLOCK POLYMERS OF ETHYLENE OXIDE AND ITS ANALOGUES WITH STYRENE

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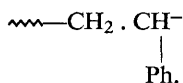
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Reactions of "living" polystyrene with ethylene oxide were investigated and it was shown that polystyrene containing hydroxylic groups on both ends can be prepared. The properties of their sodium salts and particularly their association in solution are discussed. Block polymers, containing a middle block of polystyrene and two end blocks of polyethylene oxide, can be synthesized. These materials show some unusual properties which are discussed in the paper.

Reactions involving propylene oxide and styrene oxide were also investigated. Attempts were made to characterize the products of these reactions and particularly to isolate the corresponding block polymers. Finally, the initiation of polymerization of ethylene oxide by sodium naphthalene was examined and a mechanism for this initiation was proposed.

Anionic polymerization of styrene carried out in a suitable solvent, like tetrahydrofuran, yields "living" polymers^{1,2} which are polymeric species possessing carbanions as terminal groups,



The carbanionic ends retain their reactivity almost indefinitely; they may add further monomeric units, and thus perpetuate the polymerization, or they may be reacted with suitable reagents to yield polymers with desired end-groups. In this paper the reactions of "living" polystyrene with ethylene oxide and its homologues will be discussed, and the properties of the products described.

EXPERIMENTAL

The polymerizations to be described were initiated by α -methyl styrene "tetramer". This initiator is produced by reacting a dilute solution of the monomer with metallic sodium in tetrahydrofuran at room temperature, followed by filtration from excess sodium. The dilution is such that polymerization to high-molecular-weight material is thermodynamically forbidden, and consequently the product consists of a mixture of dimers, trimers and tetramers, the last predominating under our experimental conditions. It has been shown³ that these low-molecular-weight polymers possess two terminal carbanionic end-groups capable of initiating further polymerization.

Reaction vessels used in this investigation were constructed such that each solution of "living" polymer could be divided into several portions without exposure to air. This method allows, therefore, a direct comparison of phenomena occurring as a result of various termination reactions.

TERMINATION OF "LIVING" POLYSTYRENE WITH ETHYLENE OXIDE AND ITS HOMOLOGUES

The red solution of "living" polystyrene of approximately 10,000 molecular weight was divided into two portions, one being "killed" by addition of a trace of water and the other by ethylene oxide. The red colour disappeared instantaneously in both cases.

However, the viscosity of the solution to which ethylene oxide had been added increased markedly, while no change was observed in the viscosity of the other solution on addition of water. The polymers were precipitated by pouring the colourless solutions into an excess of acidified methanol. They were then redissolved and reprecipitated twice before dissolving in dry benzene and freeze-drying in high vacuum. This purification should remove all traces of ethylene oxide, glycol and methanol. The dried samples of the purified polymers were finally dissolved in dry carbon tetrachloride and their infra-red spectra examined. The polymer terminated with ethylene oxide showed a distinct absorption at 2.9μ indicating the presence of OH groups. On the other hand, no OH groups were detected in the polymer "killed" by water. From the intensity of the OH absorption band the weight percent concentration of $-\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ groups in the former polymer was found to be approximately 2 % while the calculation based on the molecular weight and the assumption that ethylene oxide molecules add to both ends of the polymers lead to the value of about 1 %. In view of the inherent technical difficulties, this agreement is considered satisfactory giving the proper order of magnitude for the number of OH groups per polymeric molecule.

To obtain quantitative data on the number of end-groups, further samples of polymers were prepared and analyzed for active hydrogens by the Zerewitinov technique. The results, given in table 1, indicate that the determined number of OH groups per chain in the polymer "killed" by ethylene oxide is not much different from the theoretically expected value of 2.

TABLE 1.—DETERMINATION OF END $-\text{OH}$ GROUPS IN POLYMERS BY ZEREWITINOV TECHNIQUE

type of polymer	m.w. from $[\eta]$	number of OH group per polymer molecule
polystyrene A, "killed" by ethylene oxide	11,300	2.08
polystyrene A, "killed" by propylene oxide	11,300	1.85
polystyrene A, "killed" by water	11,300	none
polyethylene oxide initiated by α -methyl styrene tetramer	$\sim 10,000$	2.3

We are indebted to Mr. N. Nicholov for these analyses.

Molecular weight is calculated from the relationship, $\text{m.w.} = 2.9 \times 10^5 [\eta]^{1.5}$, Outer, Carr and Zimm, *J. Chem. Physics*, 1950, **18**, 830.

Identical intrinsic viscosities measured in toluene were obtained for polymers produced from the same stock solution by termination with water and with ethylene oxide, although the Huggins' k' parameter was slightly greater for the polymer terminated by the latter reagent (see fig. 1). This is not unexpected since some association of these polymers, caused by hydrogen bonding, is bound to occur in toluene solution. Such an association is much stronger for polymers terminated with carboxylic groups (see fig. 1) which show an even greater tendency to form hydrogen bonds. It is concluded, therefore, that the addition of ethylene oxide does not change the molecular weight of the "living" polystyrene. This conclusion seems unusual in view of the tremendous increase in the viscosity of the original solution of the "living" polymers on addition of ethylene oxide. Apparently the $\sim\sim\sim\text{CH}_2\text{O}^-$, Na^+ ion pairs strongly associate, while the association of $\sim\sim\sim\text{CH}^-$, Na^+ ion pairs is negligible. This difference in the degree of association is



probably due to the diffuse character of the negative charge in the benzyl ion in contrast to the localized charge on the $\sim\sim\sim\text{CH}_2\text{O}^-$ end. In this respect, polymers with $-\text{COO}^-$ ends show intermediate properties in agreement with the postulated dependence of the degree of association on the charge density.^{4, 5}

The association of the polymers breaks down on exposure to traces of moisture or oxygen as shown by the sharp decrease in the viscosity of the primary solution. The effect due to moisture is easily understood; water hydrolyzes alcoholates and thus polymers with hydroxylic end-groups and sodium hydroxide are formed. On the other hand, the effect of oxygen is less easily comprehended. It was demonstrated that the viscosity of the solution rapidly decreases even if the oxygen is rigorously dried and if it is introduced

in the absence of light. The latter observation excludes any possible photo-oxidation of the solute or solvent. On the other hand, no change in viscosity was observed when the polymer solution was exposed to dry and oxygen-free nitrogen.

The extent of oxidation of alkaline solution by gaseous oxygen was checked by preparing a solution of α -methyl styrene tetramer terminated with ethylene oxide. One-half of this solution was exposed to dry oxygen and vigorously stirred for 1 h and then acidified, while the other half was immediately acidified with gaseous HCl. Thereafter solvent was distilled off in vacuum, polymers redissolved in tetrahydrofuran, filtered from sodium chloride and the clear solutions submitted to infra-red analysis. The first sample showed a large peak at 1730 cm^{-1} , and none was shown by the second sample. The stretching frequency of aldehydic $\text{C}=\text{O}$ is given at $1740\text{--}1720\text{ cm}^{-2}$, hence aldehydes *are* formed on exposure to oxygen. From the intensity of the peak it was estimated that $\text{CCHO}/\text{CCH}_2\text{OH} \approx 0.05$. It is uncertain, therefore, whether this oxidation is responsible for the observed decrease in viscosity.

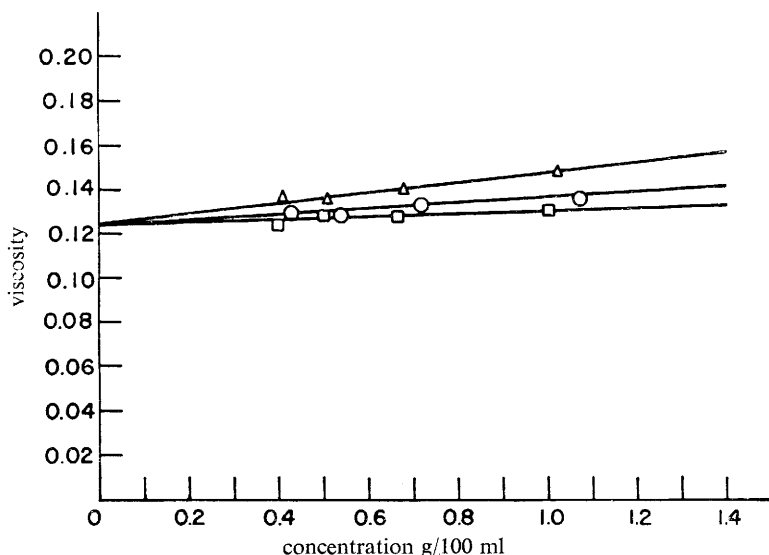


FIG. 1.

- Δ polystyrene "killed" with CO_2 .
- \circ polystyrene "killed" with ethylene oxide.
- \square polystyrene "killed" with water.

"Living" polystyrene reacts in a similar way with other cyclic oxides such as propylene oxide and styrene oxide. Addition of these compounds to the red solution of "living" polystyrene at room temperature decolorized it instantaneously. The viscosities of the resulting solutions were high although slightly lower than that of the corresponding solution reacted with ethylene oxide. This indicates that the same termination step, i.e. fission of the epoxide ring and formation of associated alcoholate negative ions, is involved in all these processes. End-group analysis by the Zerewitinov technique of two samples produced from the same "living" polystyrene but "killed" with ethylene oxide and propylene oxide respectively gave a slightly lower number of terminal OH groups per chain for the latter "killing" agent (see table 1). Apparently the tertiary hydrogen of propylene oxide reacts to some extent with the "living" ends by transferring a proton and this reaction leads to a $-\text{CH}_2 \cdot \text{Ph}$ end-group instead of a CH_2O^- group.

PREPARATION OF BLOCK POLYMERS

As shown in the preceding section, the addition of ethylene oxide produces polymers with $-\text{CH}_2 \cdot \text{CH}_2 \cdot \text{O}^-$, Na^+ end-groups. These are, of course capable of polymerizing further amounts of ethylene oxide. Therefore, addition of an excess of ethylene oxide

and subsequent heating of the resulting mixture for a sufficiently long time should result in the formation of a polymer containing a block of polystyrene between two blocks of polyethylene oxide. To investigate this possibility the following experiments were performed. Identical solutions of "living" polystyrene of about 10,000 molecular weight were mixed with ethylene oxide in weight proportions 3 : 1, 1 : 1 and 1 : 3. The mixtures were heated for a week in sealed ampoules at 75°C. The resulting mass was freed from the solvent and from any possible unreacted ethylene oxide by warming it in vacuum, and was then redissolved in benzene and freeze-dried. By weighing the residue it was found that the polymerization had proceeded quantitatively.

These polymers do not precipitate from ethyl methyl ketone solutions on addition of methanol, and even addition of water resulted only in slight turbidity. This proves the absence of homopolystyrene in the polymer. There remained, however, the possibility that homopolyethylene oxide could have been produced during the polymerization by some chain transfer mechanism. To determine whether this was so, a sample of the block polymer containing styrene and ethylene oxide in the ratio of 3 : 1 and a mixture of the corresponding homopolymers in the same weight ratio were shaken over night with cold water. To ensure complete mixing of the homopolymers the two components were dissolved in benzene and freeze-dried, and the resulting material used in the extraction experiments. It was found that only 2 % of the block polymer was water-soluble, whereas 15 % of the mixture was extracted. Moreover, u.-v. analysis of tetrahydrofuran solutions of these extracts showed the presence of aromatic peaks in the spectrum of the water-soluble fraction of the block polymer and the absence of any such peaks in the extract obtained from the mixture. From the intensity of the aromatic peaks it was calculated that the water-soluble extract of the block polymer contained about 40 % by weight of polystyrene. Apparently this extract represents the fraction of the block polymer rich in polyethylene oxide, so that the amount of homopolyethylene oxide in the original sample must be negligible.

Attempts were made to extend the technique leading to formation of block-polymers of polystyrene and polyethylene oxide to other epoxides. Experiments performed with propylene oxide led to a small increase in the weight of the resulting solid, indicating that only 25 % of the added propylene oxide polymerized under the experimental conditions giving a material which contained 10 % by weight of propylene oxide. Approximately 6 % by weight of this material was extracted by methanol, and infra-red examination of this fraction gave no evidence of aromatic moieties. It seems, therefore, that chain transfer to propylene oxide does take place during the polymerization, and the extracted material represents the homo-polypropylene oxide present in the original mixture. Its semi-liquid appearance points clearly to its low-molecular-weight nature.

Formation of a block polymer composed of polystyrene and polystyrene oxide was attempted. The results are, however, inconclusive. Again only a fraction (approximately one-quarter) of added styrene oxide polymerized; the physical appearance of the resulting product was nevertheless changed markedly. Separation of the block polymer from the homopolymer was unsuccessful so no evidence for chain transfer was obtained. However, the presence of the tertiary hydrogen adjacent to the benzene nucleus strongly suggests that chain transfer in this system is very probable.

PROPERTIES OF POLYSTYRENE + POLYETHYLENE OXIDE BLOCK POLYMERS

The styrene + ethylene oxide block polymers showed some unusual properties. Their solutions in methyl ethyl ketone and in tetrahydrofuran turns slightly cloudy when water is added, but no precipitate is formed. On the other hand, a white precipitate appears on addition of a drop of water to the clear solution of the block-polymer in benzene. Apparently, the non-hydrated polymer is soluble in benzene while the hydrated chains of ethylene oxide coagulate as result of inter-molecular hydrogen bonding.

A close inspection of this phenomenon shows that it is more complex than it first appears. Addition of a drop of water to the benzene solution of homopolyethylene oxide does not lead to precipitation of the polymer, nor is precipitation observed when water is added to a mixture of homo-polyethylene oxide and homo-polystyrene dissolved in benzene. This paradox may be explained by examining the conditions which govern precipitation phenomena. Precipitation requires the product of concentrations (or activities) of polyethylene oxide and

water in benzene to exceed some minimum value corresponding to the equilibrium in saturated solution, i.e. $n\text{H}_2\text{O} + \text{polymer} \rightleftharpoons \text{hydrated polymer}$ in saturated solution. The block polymer is insoluble in water. Hence, on addition of water to the benzene solution of the block polymer, the chemical potential of water remains essentially unchanged, and thus the concentration of water in the benzene layer is a maximum. Homo-polyethylene oxide is water-soluble, hence addition of water to its solution in benzene leads to the partition of the polymer between these two phases. Consequently, in the latter case the water layer consists of an aqueous solution of polyethylene oxide so that the chemical potential of water is lowered and its concentration in the benzene phase decreases accordingly. Apparently, this decrease in the concentration is sufficient to prevent the precipitation of the hydrated polymer.

The validity of this explanation was proved by adding a drop of concentrated aqueous NaI solution to the benzene solution of the block polymer. No precipitate was formed although precipitation did occur when a saturated aqueous solution of NaCl was added. These experiments demonstrate that the concentration of water in benzene must exceed some minimum value to produce the new solid phase.

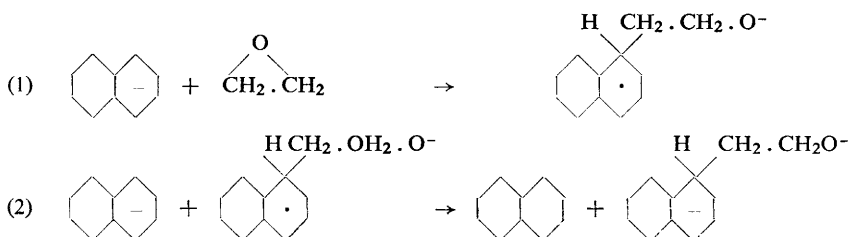
Samples of the block-polymers can be easily fused and produce a nearly transparent mass on solidifying. Nearly transparent films are also formed on casting the block polymer from toluene solution. This transparency is further evidence for the absence of homo-polymers since homo-polyethylene oxide which has been melted yields an opaque mass due to crystallization of the polymer and fusion of a mixture of polystyrene and polyethylene oxide give a white mass indicating the incompatibility of the homo-polymers.

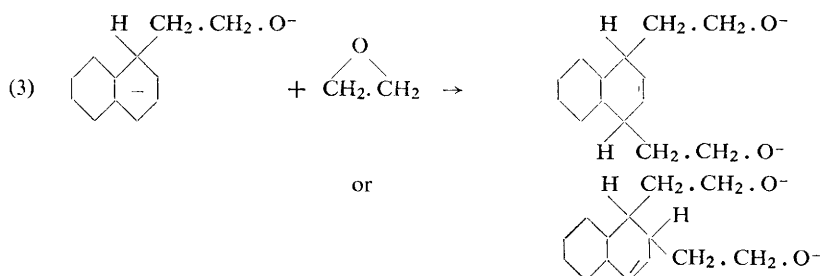
Since the block polymers possess two terminal OH groups per molecule, they may be linked together to form poly-block polymers. For example, heating their toluene solution with adipinyl dichloride or adding phosgene to the original alkaline solution links, the polymeric molecules into larger linear aggregates. In some experiments this procedure increased the molecular weight of the product by factor of 5-6.

HOMO-POLYMERIZATION OF ETHYLENE OXIDE

It follows from the method of preparation of block polymers that the benzyl ion is an efficient initiator of ethylene-oxide polymerization, and the reaction proceeds smoothly and without complications due to chain transfer in tetrahydrofuran. It was expected, therefore, that solution of "living" α -methyl styrene "tetramer" should initiate homo-polymerization of ethylene oxide, and indeed quantitative conversion of this monomer to polymer was observed with this initiator.

Polymerization of ethylene oxide was also initiated by the green solution of sodium naphthalene. This reaction may proceed in two ways: either through an electron transfer process to ethylene oxide^{1,2} which would produce a negative ethylene oxide radical-ion and eventually the $^-\text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2\text{O}^-$ di-ion, or by reaction involving addition to sodium naphthalene.^{6,7} The course of the latter reaction may be represented by the following equations:





The di-ions formed in reaction (3) then continue the propagation.

To distinguish between these two alternative mechanisms the homo-polyethylene oxides obtained by initiating the reaction with α -methylstyrene tetramer, sodium naphthalene and sodium ethoxide were examined. The u.-v. spectra of these polymers are shown in fig. 2. No absorption is observed in the polymer

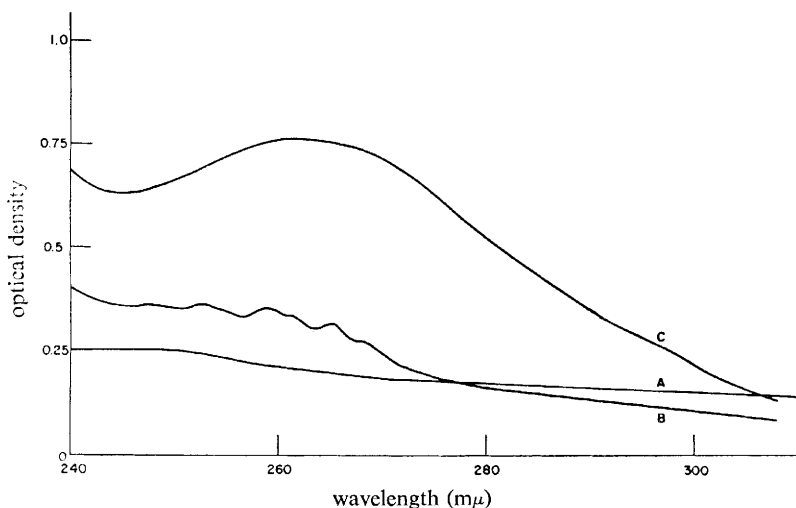
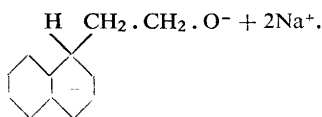


FIG. 2.—U.-v. spectra of polyethylene oxides. A, initiated by sodium ethoxide; B, initiated by α -methyl styrene tetramer disodium; C, initiated by sodium naphthalene.

initiated by sodium ethoxide (curve A); the peaks characteristic for aromatic derivatives are shown in the polymer initiated by α -methylstyrene tetramer (curve B), and a broad peak characterizing 1:2-dihydro-naphthalene shows in the polymer initiated by sodium naphthalene (curve C). Hence, the initiation by sodium naphthalene seems to proceed primarily by the addition reaction described by eqn. (1), (2) and (3).

This mechanism is further supported by the following observation. When a small excess of ethylene oxide was reacted with a solution of sodium naphthalene at -80°C a precipitate was produced which partially dissolved on warming to form a red solution. This colour disappeared when the temperature was raised further and eventually a colourless solution containing a white precipitate was produced as room temperature was reached. These results may be interpreted in the following way. At -80°C ethylene oxide reacted with sodium naphthalene according to eqn. (1) and (2) slowly giving the insoluble red salt



On raising the temperature the red ions reacted with more ethylene oxide to form eventually the white insoluble salt of dihydronaphthalene di-epoxide.

When only 1/2 mole equivalent of ethylene oxide was added at -80°C to sodium naphthalene the red precipitate remained even at room temperature due to the absence of ethylene oxide. Approximate spectroscopic measurements indicate that the ratio of 1 : 2 dihydro-compound to 1 : 4 dihydro-compound is about 1 : 4.

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¹ Szwarc, Levy and Milkovich, *J. Amer. Chem. Soc.*, 1956, **78**, 2656.

² Szwarc, *Nature*, 1956, **178**, 1168.

³ Ladacki, Waack and Szwarc, unpublished results.

⁴ Brody, Richards and Szwarc, *Chem. and Ind.*, 1958, **45**, 1473.

⁵ Honing and Singeltery, *J. Physic. Chem.*, 1956, **60**, 1114.

⁶ Scott, Walker and Hansley, *J. Amer. Chem. Soc.*, 1936, **78**, 2656.

⁷ Paul, Lipkin and Weissman, *J. Amer. Chem. Soc.*, 1956, **78**, 116.