Block polymers from poly(ethylene oxide) and styrene

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Block copolymers containing poly(ethylene oxide) and polystyrene segments were synthesised via chemical reactions. A step-wise procedure was first employed to prepare peroxycarbamates which were later used to initiate free radical polymerization of styrene at elevated temperatures. In some runs the polymerization temperature and time were programmed. Styrene contents, molecular weights, elastic modulus–temperature relationships, impact strengths and stress–strain behaviour of the copolymers were determined.

INTRODUCTION

In recent years there have been various attempts to prepare block copolymers via chemical reactions using certain intermediate prepolymers and other monomeric compounds. The aim has been to synthesise prepolymeric peroxycarbamates which could be used as initiators for the free radical polymerization of a vinyl monomer at elevated temperatures.

In 1972, Baysal *et al.*[1] described the synthesis and characterization of some new polymeric peroxycarbamates. These were prepared by successive reaction of poly(ethylene oxides), first with bis(4-isocyanatocyclohexyl)methane and then with 2,5-dimethyl-2,5-dihydroperoxyhexane or with cumene hydroperoxide. Depending on the initial reaction conditions, 4 different initiators were obtained. One of them was used in a kinetic investigation of the initiation of polymerization of styrene at 80°C.

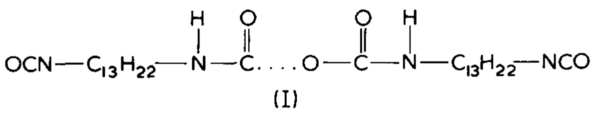
Synthesis and characterization of block copolymers of styrene and methyl methacrylate with butadiene, ethylene oxide and propylene oxide have been described[2,3]. These copolymers were prepared by using two different procedures. In the step-wise procedure, a peroxycarbamate was first prepared. This intermediate product was later used to initiate the polymerization of a vinyl monomer at elevated temperatures. In the second procedure, the peroxycarbamate was synthesised *in situ* using the vinyl monomer as the solvent. The mixture then was heated in order to obtain the copolymer. It should be added that the polymerization temperature was programmed in some of the runs. Details of the temperature programming have been described previously[4].

In this work, copolymers of styrene and ethylene oxide were prepared. This method is based on the following sequence of reactions.

Step 1

$$HO\ldots\ldots OH \quad + \quad \begin{matrix}>2\\ \text{or}\\ 1{\cdot}1\end{matrix}\ OCN{-}C_{13}H_{22}{-}NCO \rightarrow$$

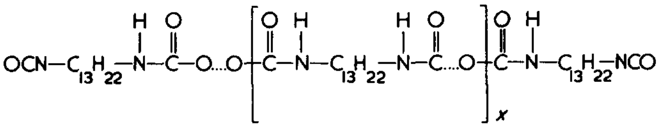
Poly(ethylene oxide) glycol
Prepolymer Diisocyanate



$$OCN{-}C_{13}H_{22}{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}\ldots O{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}C_{13}H_{22}{-}NCO$$

(I)

or



$$OCN{-}C_{13}H_{22}{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O\ldots O{-}\left[\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}C_{13}H_{22}{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}\ldots O\right]_x{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}C_{13}H_{22}{-}NCO$$

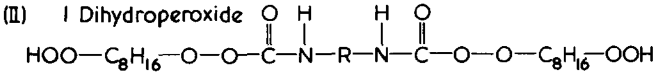
(II)

(I) is the main product when more than 2 mol of the diisocyanate are used[4] in Step 1. (I) is an isocyanate-capped prepolymer with hardly any chain extension. (II) results when 1.1 mol of the diisocyanate is used in Step 1. (II) is an isocyanate-capped polymer with some chain extension.

Step 2

$$\begin{matrix}(I)\\ \text{or}\\ (II)\end{matrix}\ + \ \begin{matrix}>2\\ \text{or}\\ 1\end{matrix}\ HOO{-}C_8H_{16}{-}OOH \rightarrow$$

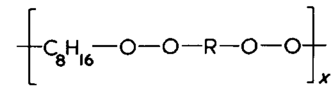
Dihydroperoxide



$$HOO{-}C_8H_{16}{-}O{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}R{-}\overset{H}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}O{-}C_8H_{16}{-}OOH$$

(III)

or



$$\left[{-}C_8H_{16}{-}O{-}O{-}R{-}O{-}O{-}\right]_x$$

(IV)

Here R represents the diisocyanate and the prepolymer residues of the chain combined through urethane linkages. (III) is the main product when more than 2 mol of the dihydroperoxide are used in Step 2. (III) is a diperoxycarbamate which can be used as an initiator for the free radical polymerization of a vinyl monomer. (IV) results when 1 mol of the dihydroperoxide is used in Step 2. (IV) is a polyperoxidic initiator for vinyl polymerization.

Formation of (III) and (IV) can be greatly accelerated by adding a catalyst, such as dibutyltin dilaurate, to the reaction mixture in Step 2.

Step 3

In this step, either (III) or (IV) is used to initiate the free radical polymerization of styrene at elevated temperatures.

Using the above sequence of reactions, several peroxycarbamates were prepared and used to get block copolymers of styrene and ethylene oxide. Mechanical and physical characterization of the products were carried out.

EXPERIMENTAL

Materials

Poly(ethylene oxide) glycols (PEG-4000 and PEG-20000) were products of Fluka A. G. The molecular weight of PEG-4000 was 4450 (from vapour pressure osmometry) and that of PEG-20000 was 19300 (from viscometry). They were dried at 70°C for 1 h under reduced pressure before use.

Bis(4-cyanatocyclohexyl)methane was a product of Du Pont de Nemours and Co. It was distilled under reduced pressure before use. Its purity, determined by isocyanate analysis, was better than 99%.

2,5-Dimethyl-2,5-dihydroperoxyhexane was a product of Lucidol Division, Penwalt Corp. It was recrystallized from carbon tetrachloride. Peroxygen content was 97% of the theoretical value.

Styrene was a product of Fluka A. G. It was washed with 5% NaOH solution and H_2O, dried with $CaCl_2$ and freshly distilled under reduced pressure before use (b.p. 41°C at 2400 N/m^2).

Chloroform, toluene, benzene, dichloromethane, 1,2-dichloroethane and petroleum ether were products of Merck A. G. These were used after drying with 4X molecular sieves.

Dibutyltin dilaurate (T-12) was a product of Cincinnati Milacron Chemicals Inc. and was used without any purification.

Methanol was supplied by Kromekto Laboratories and was used without any purification.

Procedure

Preparation of peroxycarbamates. The prepolymer and the diisocyanate were reacted at 80°C in bulk under a blanket of dry nitrogen. The molar ratio of the diisocyanate to the prepolymer was either more than 2.0 or 1.1 and the reaction period was over 22 h. The resulting product was dissolved in dichloromethane, precipitated in a large excess of fresh petroleum ether and dried *in vacuo* at 25°C for 15 h. Molecular weight of the product was determined by vapour pressure osmometry (Mechrolab Vapour-Phase Osmometer, Model 301A). This product was later dissolved in dichloromethane or 1,2-dichloroethane and a calculated amount of the dihydroperoxide was added together with a few drops of T-12. The mixture was reacted under dry nitrogen at room temperature in the dark for over 48 h. The resulting peroxycarbamates were isolated by precipitating in petroleum ether and drying *in vacuo* at room temperature. The molecular weights of the peroxycarbamates were either determined by vapour pressure osmometry, estimated from their peroxygen contents or determined by viscometry using the relationship:

$$[\eta] = 48 \times 10^{-5} \bar{M}_n^{0.68}$$

for benzene solutions at 20°C[5]. These peroxycarbamates were soluble in methanol.

Initial conditions employed for the preparation of 6 peroxycarbamates and their molecular weights and peroxygen contents are given in *Table 1*.

Synthesis and characterization of copolymers. These 6 peroxycarbamates were used in the synthesis of 19 copolymers. 11 of these copolymers were prepared in bulk, while the rest were synthesised in solution, followed by subsequent precipitation in a suitable non-solvent.

Weighed amounts of the peroxycarbamates were dissolved in predetermined amounts of styrene. Benzene was added to the mixture in some runs as the polymerization solvent. The mixture was then either degassed on the vacuum line (ultimate pressure 1.3×10^{-4} N/m^2) or was blanketed with dry nitrogen gas. The solution was placed in thermostatically controlled baths and polymerization was carried out for desired periods of time. The products obtained in bulk polymerizations were then dissolved in chloroform. Large volumes of methanol or petroleum ether were later used as 'precipitants' for the products obtained. The copolymers were dried *in vacuo* at 50°C for 15 h.

Styrene content of the copolymers was determined by u.v. spectroscopy at 269 mμ[6]. This method is based on measuring the absorbance of pure polystyrene, peroxycarbamate and copolymer at 269 mμ. From the measured values of the absorbances, the weight percentage of styrene in the copolymer can be calculated by using the equation:

$$\% \text{ Styrene} = \left(\frac{\epsilon_c - \epsilon_{pc}}{\epsilon_{ps} - \epsilon_{pc}} \right) \times 100$$

where ϵ_c, ϵ_{pc} and ϵ_{ps} are specific extinction coefficients of the copolymer, peroxycarbamate and polystyrene, respectively. Molecular weights of the copolymers were determined by viscometry via the following equations: Runs 1–5, $[\eta] = 44 \times 10^{-5} \bar{M}_n^{0.65}$ given for toluene solutions at 25°C[7]; Runs 6–19, $[\eta] = 4.61 \times 10^{-3} \bar{P}_n^{0.73}$ given for benzene solutions at 30°C[8].

For mechanical tests, samples were compression moulded and annealed at 105°C for 24 h. Stress–strain tests were carried out on an Instron machine at room temperature with a rate of elongation of 5×10^{-4} m/min. Torsional modulus–temperature relationships of the copolymers were established by means of a Gehman Torsion Tester. Impact strengths of notched specimens were measured on a Hounsfield Plastic Impact Machine, a Charpy-type instrument, at room temperature.

I.r. spectra of compression moulded films were taken on a Perkin–Elmer 177 Grating Spectrophotometer.

RESULTS AND CONCLUSIONS

Using the above described 6 peroxycarbamates, 19 copolymers of styrene and poly(ethylene oxide) were synthesised. *Table 2* contains the initial conditions, and other related data, of the first 11 bulk polymerizations. Runs 10 and 11 were carried out under a nitrogen blanket while the rest were *in vacuo*. 4 of the 6 peroxycarbamates were used in these 11 polymerizations and these are indicated in the

Table 1 Preparation of peroxycarbamates

Peroxy-carbamate no.	(Hylene W) / (Prepolymer)	(–OOH) / (–NCO)	Peroxygen content (%)	Molecular weight
1	2.0	>2	3.10	5540[a]
2	1.1	>2	0.318	40 250[b]
3	1.1	>2	0.310	41 250[b]
4	1.1	1.0	–	–
5	1.1	1.0	1.07	–
6	3.42	>2	–	20 900[c]

[a] Determined from vapour pressure osmometry. [b] Estimated from peroxygen content, assuming 4 peroxygen groups per molecule. [c] Estimated from viscometric measurements

Table 2 Preparation of styrene and PEG copolymers in bulk

Run no.	PC[a]	Peroxycarbamate (wt%) Initial	Peroxycarbamate (wt%) Found[b]	Polymerization Time (h)	Polymerization Temp.(°C)	Conversion (%)	$[\eta]$ (dl/g)	$\bar{M}_n \times 10^{-3}$	Remarks
1	1	4.9	6.2	39	80	100	0.964	138	–
2	2	7.3	4.3	39	110	83.2	0.495	49.5	–
3	2	9.6	4.7	39	110	83.4	0.493	49	–
4	2	14.1	15.6	39	110	79.6	0.518	53	–
5	2	7.7	10.5	39	110	91.7	0.505	51	–
6	3	26	–	67	80	73	–	–	–
7	3	12	9.1	67	80	76	1.382	257	–
8	3	44	40.2	67	80	46	1.306	238	–
9	3	19	19.2	67	80	79	1.419	266	–
10	6	25.0	30.1	65	80	76.1	1.625	321	Under N_2
11	6	7.0	16.6	65	80	89.7	2.300	517	Under N_2

[a] PC represents peroxycarbamate. [b] These values were obtained by subtracting the weight percentage of styrene from 100

Table 3 Preparation of styrene and PEG copolymers in benzene

Run no.	PC[a]	Peroxycarbamate (wt%) Initial	Peroxycarbamate (wt%) Found[b]	Polymerization Time (h)	Polymerization Temp. (°C)	Conversion (%)	$[\eta]$ (dl/g)	$\bar{M}_n \times 10^{-3}$	Remarks
12	3	48.7	34.3	143	80	34.6	–	–	–
13	3	8.0	3.6	94	80	90.2	–	–	–
14	4	13.0	16.5	72	80	65.9	0.948	153	–
15	4	12.7	10.8	72	80	76.6	1.120	193	Under N_2
16	4	48.1	–	72	80	–	0.260	26	–
17	4	27.1	11.7	134.5	80	59.3	0.550	73	–
18	5	13.1	18.2	4.63	80.93	87.6	0.680	98	Under N_2
19	5	48.8	–	4.63	80.93	76.9	–	–	Under N_2

[a] PC represents peroxycarbamate. [b] These values were obtained by subtracting the weight percentage of styrene from 100

second column of the Table. The weight percentage of the soft material incorporated into the polymeric product ranged from 4.3 to 40.2%.

Examination of the data recorded in *Table 2* leads to some generalities presented by the systems described in this Table. Higher polymerization temperatures led to an expected decrease in the molecular weight of the final copolymers containing nearly the same proportion of the soft material (compare Runs 5 and 7). Another generality is that as the proportion of the soft material incorporated into the polymeric chain increases the overall conversion of the initial mixture to polymer decreases. Furthermore, Runs 2–5 indicate that as the soft material proportion increases in the copolymer the molecular weight of the final product increases slightly.

Table 3 contains the initial conditions and other data related to polymerizations in solution. 3 of the above described 6 peroxycarbamates were used in the synthesis of 8 copolymers in benzene. Runs 15, 18 and 19 were carried out under nitrogen while the rest were *in vacuo*. It should be noted that also in the solution polymerizations conversion decreased with increasing soft material content of the final copolymer. Comparing Runs 15 and 17 leads to the conclusion that the molecular weight of the final copolymer is substantially higher if the polymerization is carried out under nitrogen.

The polymerization temperature in Runs 18 and 19 was programmed. Polymerization was started at 80°C and ended at 93°C. Theoretical considerations forming the basis of this temperature programming procedure have been given previously[4]. The aim of this procedure is to use more than one polymerization temperature in order to obtain a size distribution of the vinyl blocks with no unreacted peroxidic groups left embedded in the copolymer. The procedure is based on finding a suitable temperature at which the rate of the disappearance of the initiator is approximately the same as the rate of the consumption of the vinyl monomer.

Examination of the data presented in *Table 4* reveals why 93°C was chosen as the upper temperature for Runs 18 and 19. The data given in this Table were derived from determining[9] the rate of decomposition of a peroxycarbamate similar to the ones used in this work. At 93°C (1/*e*) life of the initiator decomposition is approximately equal to the (1/*e*) life of monomer consumption.

In the infra-red spectra of the polymers peaks at around 3300 cm^{-1} were observed in all runs. This absorption is due

Table 4 Temperature programming for copolymerization reactions

Temperature (°C)	k_d (sec^{-1})	$1/k_d$ (sec)	τ[a] (sec)
25	2.43×10^{-9}	4.12×10^{8}	5.18×10^{6}
40	3.97×10^{-8}	2.52×10^{7}	9.25×10^{5}
50	2.21×10^{-7}	4.52×10^{6}	3.22×10^{5}
60	1.11×10^{-6}	8.98×10^{5}	1.29×10^{5}
70	5.11×10^{-6}	1.96×10^{5}	4.84×10^{4}
80	2.15×10^{-5}	4.66×10^{4}	2.09×10^{4}
90	8.33×10^{-5}	1.20×10^{4}	9.87×10^{3}
93	1.24×10^{-4}	8.10×10^{3}	8.07×10^{3}
95	1.60×10^{-4}	6.25×10^{3}	7.08×10^{3}
100	3.01×10^{-4}	3.32×10^{3}	5.17×10^{3}
110	1.02×10^{-3}	9.84×10^{2}	4.11×10^{3}

[a] τ is (1/*e*) life for monomer consumption

to the $\underset{\mathrm{H}}{\underset{|}{-\mathrm{N}-}}$ stretching in the $-\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-$ group of the peroxycarbamate. Presence of this absorption peak in the spectrum indicates the incorporation of the peroxycarbamate in the copolymer chain which constitutes proof for block polymer formation.

In *Figure 1* elastic modulus–temperature relationships of some of the copolymers prepared in the bulk are reproduced. This Figure also contains the same relationship for a polystyrene sample. Random copolymers have sharp transition temperatures while block and graft copolymers exhibit a slow decrease in the elastic modulus over a wide range of temperature[10,11]. It should be mentioned that although copolymers 7–9 contained varying amounts of soft material, the transition temperatures (T_i) for these polymers, as estimated from the curves in *Figure 1*, were essentially the same, about 95°C. A similar trend was also found for propylene oxide–methyl methacrylate block polymers prepared by a one-shot, temperature programmed procedure[3]. T_i values of other copolymers studied were also around 95°C.

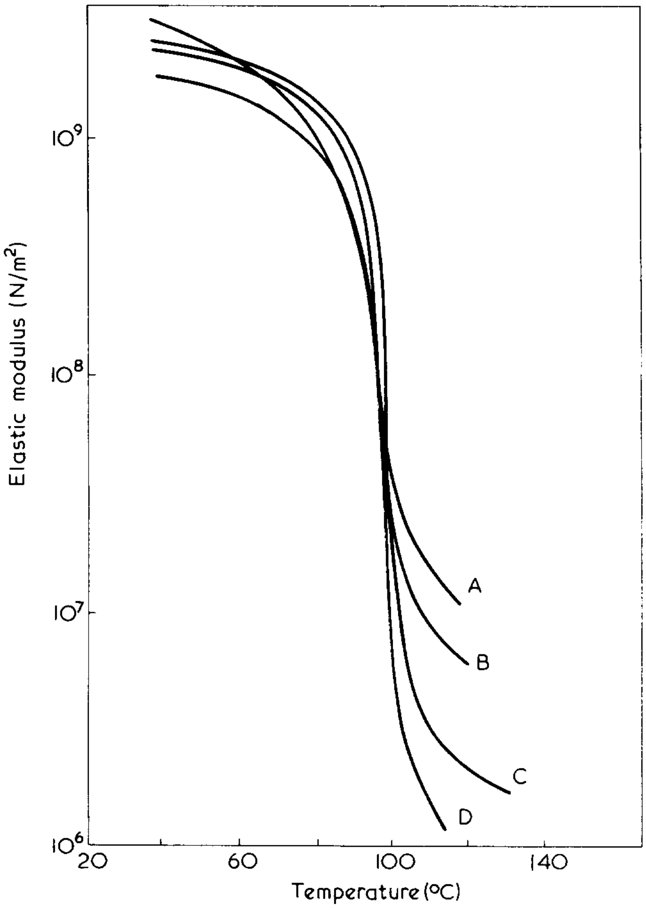


Figure 1 Elastic modulus–temperature relationship for various copolymers. Run numbers (listed in *Tables 2* and *3*): A, 7; B, 9; C, 8; D, PS

Results of stress–strain tests and impact strength measurements are given in *Table 5*. Ultimate elongations for all copolymers studied were essentially the same although they contained differing amounts of the peroxycarbamate. This is in line with observing essentially the same transition temperature for these copolymers. This behaviour is of course an anomaly. It could well be that the stress bearing part in the copolymer is the polystyrene blocks irrespective of the presence of the soft material in the chain. Further mechanical and morphological studies are under way in order to clarify this point. As far as the impact strength is concerned there is a definite but slight improvement with increasing soft material content.

Evidence of gas evolution during the course of polymerization was observed in this work, although the nature of the gas was not investigated. Certain authors[12] have also reported loss of CO_2 from peroxycarbamates used in vinyl polymerization, although others have reported[13] no such loss. It is probable that different peroxycarbamates behave differently in this respect.

It may be anticipated that polymerization in such a system would inevitably result in the formation of pure homopolymer. This homopolymer would, of course, remain in the final polymer and effective fractionation methods would have to be developed to separate the homopolymer from the copolymer. It should be mentioned that evidence against homopolymer formation was obtained in this work when a polymeric peroxycarbamate (PC no. 4 and 5) was used as the initiator. The products obtained in Runs 16 and 19 did not precipitate in a large excess of methanol, indicating that no detectable homopolymer was formed during the polymerization. Since the precipitant in these runs was petroleum ether, the final product is bound to contain the unreacted peroxycarbamate.

As a concluding remark, it may be stated that this method of copolymer synthesis is effective in producing block polymers with high yields and within reasonable polymerization times.

Table 5 Mechanical tests with PEG and styrene copolymers

Run no.	Soft material (%)	Relative impact strength	Youngs' modulus × 10^{-8} (N/m^2)	Ultimate elongation (%)	Ultimate strength × 10^{-7} (N/m^2)	Ultimate modulus × 10^{-8} (N/m^2)
1	4.9	1.08	9.31	4.2	3.02	7.21
7	9.1	1.09	9.22	4.2	2.98	7.14
8	40.2	1.29	6.70	4.3	2.19	5.11
9	19.2	1.18	7.69	4.2	2.49	5.99
10	30.1	1.43	–	–	–	–
11	16.6	1.86	–	–	–	–
14	16.5	1.30	–	–	–	–
18	18.2	0.57	–	–	–	–
Polystyrene ($\bar{M}_n$ = 1.36 × 10^5)	–	1.00	–	–	–	–

ACKNOWLEDGEMENTS

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