

Preparation of Polystyrene-Block-(Ethylene Oxide)s and Characterization of the Products

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Synopsis

Block copolymers containing segments of poly(ethylene oxide) and polystyrene were synthesized. Dihydroxyl-terminated polyethers (PEG-4000 and PEG-20,000) were reacted with an aliphatic diisocyanate (3-isocyanatomethyl-3,5,5-trimethyl-cyclohexyl-isocyanate) and with an aliphatic hydroperoxide (*t*-butyl hydroperoxide). The resulting polymeric peroxy carbamates were used as free radical initiators for vinyl polymerization. Formation of block copolymers was illustrated by several characterization methods such as chemical and UV analysis, infrared spectroscopy, and DSC thermograms. Mechanical characterization of the copolymers was made on the basis of the stress-strain curves obtained from a mechanical testing instrument (Tensilon).

INTRODUCTION

The potential of block copolymers has begun to be appreciated after the development of polyurethanes. The preparation of linear polyurethanes composed of soft polyester segments and hard polyurethane sequences was reported 30 years ago.¹ The synthesis of well-defined block copolymers from the point of view of molecular architecture was secured after the development of controlled living-anionic polymerization techniques.² An extensive review of block copolymer synthesis covering various procedures including coupling reactions between the segments containing adequate functional groups was published.³

Recently various oligomers, copolymers, and interpenetrating networks have been prepared by using prepolymers of diols, diisocyanates, hydroperoxides, and azo-compounds containing functional groups.⁴⁻⁹

A project concerning a new type of block copolymer synthesis was carried out in our laboratories. It is based on the chemical combination of low molecular weight inherently soft, rubbery polymers such as propylene oxide, with thermoplastic polymers of basically glassy properties such as polystyrene or a similar vinyl polymer. Several papers were published to describe various modes of preparation and characterization of these block copolymers.¹⁰⁻¹⁷ The copolymers were prepared by using two different procedures. In the stepwise procedure, a polymeric peroxy carbamate or a diperoxy carbamate was first prepared. This intermediate product was subsequently used to initiate the polymerization of a vinyl monomer at elevated temperatures. In the other procedure, peroxy carbamates were synthesized using the vinyl monomer as the solvent. The mixture was then heated in order to obtain the copolymer.

In this work, copolymers of styrene and ethylene oxide were prepared by using the stepwise polymerization technique. For this purpose, commercially available low and high molecular weight dihydroxyl-terminated prepolymers

were first end-capped with an aliphatic diisocyanate. The resulting intermediates were then reacted with an aliphatic hydroperoxide. The diperoxycarbamates prepared according to the preceding stepwise procedure were used as the free radical initiator for styrene polymerization.

The copolymers were characterized by physical methods and by mechanical and thermal analysis.

EXPERIMENTAL

Materials

Poly(ethylene oxide) glycols (PEG) (from Union Carbide Company), Carbowax-4000 (PEG-4000), and Carbowax-20,000, of molecular weights 4000 and 20,000, respectively, were used after drying *in vacuo* at 70°C for 3 h. 3-Isocyanatomethyl-3,5,5-trimethyl-cyclohexyl-isocyanate (IPDI) (from Fluka A. G.) was used without further purification. The purity, determined by isocyanate analysis, was 95.1%. *t*-Butyl hydroperoxide (*t*-BHP) (from Fluka A. G.) was distilled under reduced pressure. The peroxide content was found equal to 93.3%. It was used after drying over anhydrous magnesium sulfate. Dibutyltin-dilaurate (T-12) (from Fluka A. G.) was used as catalyst.

Styrene (from PETKIM Petrochemical Company, Izmit, Turkey) was made free of inhibitor by treating with 10% aqueous sodium hydroxide. It was washed with water several times, and after drying overnight with anhydrous calcium sulfate, it was fractionally distilled *in vacuo*. Solvents were carefully dried over molecular sieves (Linde Type 5A) (from Davison Chemical Company), followed by fractional distillation.

Polystyrene (from Union Carbide, SMD 3500) was used as reference material for mechanical tests. Its number average molecular weight was measured by membrane osmometer, at 35°C, in toluene ($\bar{M}_n = 9.7 \times 10^4$).

Analyses

Isocyanate analyses were performed by reacting a weighed amount of the material with standard dibutylamine solution in toluene and back titrating the excess amine with standard HCl.¹⁸ Peroxide contents were determined by standard iodometric methods.¹⁹ The polystyrene content was measured by UV spectrometry on a Shimadzu Corp. UV-150-02 Model double beam UV/VIS spectrometer. Number average molecular weights of the polymers were determined using Knauer electron membrane osmometer, equipped with regenerated fine cellulose membranes conditioned for toluene. Gel permeation chromatographs (GPC) were obtained on a TOYO SODA HPLC CCCP & 8000 instrument (TSK Gel G-2000, G-2500, G-3000 columns) using tetrahydrofuran at 35°C with flow time of 1000 $\mu\text{L}/\text{min}$. IR spectra were collected on a Pye Unicam SPI025 Model grating IR spectrometer by using a KBr crystal coated with methylene chloride solutions of the samples. DSC thermograms were obtained by a DuPont Instrument 990 DTA-DSC; heating rate was 20°C/min, under nitrogen atmosphere. Mechanical testing samples were prepared by compression molding methods, using a hydraulic press that was a product of Pasadena Hydraulics Inc. Molded samples were chipped into dumb-bell shape in the dimen-

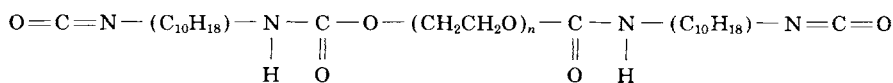
sions of 1.135 by 2.045 by 5.620 mm, using a Tensilkut, which was a product of Sieburg Industries, Inc. Stress-strain curves were obtained on at least three molded samples for each copolymer on a SS-105D-B-VTMII Model tensilon Toyo Measuring Instruments Co., with a crosshead speed of 1 mm/min and a chart speed of 200 mm/min. Hardness of the copolymers were measured on a Karl Frank GmbH Härteprüfgerät 39209, on Shore D scale.

Procedure

Preparation of Peroxycarbamates

The hydroxyl-terminated prepolymer (PEG-4000) and the aliphatic diisocyanate (IPDI) were reacted at 80°C in bulk under a blanket of dry nitrogen. This reaction was carried out with (PEG-20,000) in benzene solution under the same conditions as mentioned previously. The molar ratio of diisocyanate to prepolymer was taken to be three or more, in order to prevent undesired chain extension. The resulting product was dissolved in a suitable solvent, precipitated in a large excess of freshly distilled dry petroleum ether, filtered, and dried *in vacuo* at 25°C for 15 h. 1,2-dichloroethane was chosen as the solvent after reaction in the bulk. The reactions between dihydroxyl-terminated polyethers and aliphatic diisocyanates were studied in detail in our earlier research.^{10,11} The chain extension and coupling reactions were negligible under the experimental conditions chosen. The isocyanate content of the end-capped products were determined by end group titration of isocyanates.¹⁸ The calculated molecular weights are given in Table I.

The structural formula of the product is

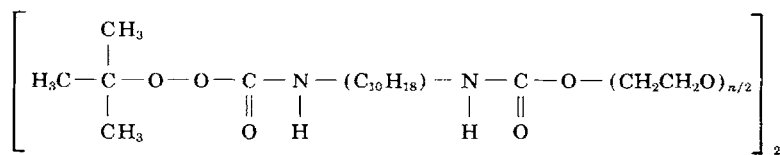


(I)

where n depends on the molecular weight of poly(ethylene oxide).

In the second step, the diisocyanate-terminated urethane was reacted with *t*-butyl hydroperoxide in methylene chloride. A few drops of T-12 catalyst was added to the reaction mixture. The reaction was carried out under a nitrogen blanket, at room temperature, in the dark, for 100 h. The molar ratio of *t*-butyl hydroperoxide to urethane ($-\text{OOH}/-\text{NCO}$) was approximately 3 in order to prevent undesired chain extension. The resulting peroxycarbamates were isolated by precipitating in petroleum ether; they were filtered and dried *in vacuo* at room temperature. Their molecular weights were calculated from their peroxide contents. The preparation conditions, the results of peroxide analysis, and the calculated molecular weights of peroxycarbamates are also given in Table I.

The structural formula of the peroxycarbamate is:



(II)

TABLE I
Preparation Conditions and Characterization of the Peroxycarbamates^a

Peroxycarbamate number	$M \times 10^{-3}$ of PEG	$\frac{[-\text{NCO}]}{[\text{PEG}]}$	$M \times 10^{-3}$ of IPDI capped PEO	$\frac{[-\text{OOH}]}{[-\text{NCO}]}$	Peroxide weight %		$M \times 10^{-3}$ of peroxycarbamates
					Calculated	Experimental	
PC-I	4	3.1	4.64	3.1	1.38	1.4	4.5
PC-II	4	3.9	4.42	3	1.38	1.4	4.5
PC-III	4	3.0	4.42	3	1.38	1.4	4.5
PC-IV	20	3.0	19.5	3	0.31	0.30	21
PC-V	20	3.2	19.1	4	0.31	0.31	21
PC-VI	20	3.0	19.5	3	0.31	0.31	21

^a M : Number average molecular weight.

TABLE II
Preparation of Styrene and Ethylene Oxide Copolymers

Run number	PC ^a number	Initial (wt %)		Found (wt %) styrene content	Polymerization		Conversion (%)	[η] (dL/g)	Molecular weight		Remarks
		PC	Styrene		Time (h)	Temp. (°C)			$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	
1	1	5.0	95.0	96.0	73; 23	80; 93	95.5	2.128	4.66	—	Bulk
2	2	10.5	89.5	91.4	4; 109	80; 93	65.0	1.402	2.45	1.10	Bulk
3	3	10.0	90.0	87.8	63	80	87.5	1.290	2.16	—	Solution
4	2	15.0	85.0	86.4	4; 109	80; 93	50.2	1.110	1.71	0.75	Solution
5	2	30.8	69.2	74.3	4; 109	80; 93	54.7	0.757	0.96	—	Bulk
6	2	28.3	71.7	69.2	4; 109	80; 93	56.2	0.632	0.72	—	Solution
7	4	10.0	90.0	95.5	134	80	87.0	2.920	7.58	—	Bulk
8	5	5.0	95.0	92.4	14; 120	80; 93	98.7	1.510	2.75	1.61	Solution
9	5	10.5	89.6	84.6	6; 120	80; 93	80.1	1.250	2.06	—	Solution
10	6	19.7	80.3	84.0	4; 94	80; 93	59.0	1.243	2.04	—	Solution
11	5	39.4	60.6	66.0	14; 120	80; 93	44.0	0.682	0.81	0.59	Solution
12	5	44.8	55.2	63.5	6; 120	80; 93	67.2	0.574	0.62	—	Solution

^a PC represents peroxydicarbonate.

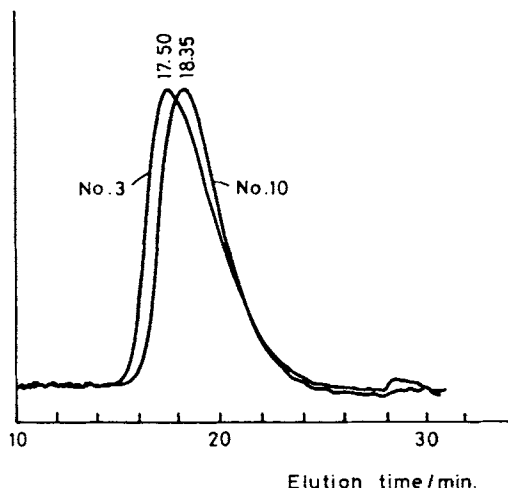


Fig. 1. GPC results of copolymer 3 (12.3% PEG-4000) and 10 (16.0% PEG-20,000).

Synthesis and Characterization of Copolymers

These peroxy-carbamates were used as initiators for the synthesis of copolymers. Four of these copolymers were prepared in bulk, while the others were synthesized in toluene solution, with subsequent precipitation in methanol. Weighted amounts of the peroxy-carbamates were dissolved in predetermined amounts of styrene. Toluene was added to the mixture as the polymerization solvent. The mixture was then degassed on a vacuum line (1.33×10^{-2} N/m²). The solutions were distributed in Pyrex tubes immersed in thermostatically controlled baths, and polymerization was carried out for the desired period of time. The solid products were dissolved in toluene and then precipitated in large volumes of methanol. Only unreacted peroxy-carbamate or styrene monomer was dissolved in methanol. The copolymers were filtered and dried *in vacuo* at 50°C for 15 h. The polystyrene, either as homopolymer or as copolymer, has not been detected in the methanol solution.

The styrene contents of the copolymers were determined by UV spectroscopy at 269 m ($37,100$ cm⁻¹). This method is based on the determination the UV absorbances of pure polystyrene, of peroxy-carbamate, and of the copolymer at that wavelength in chloroform.²⁰

Molecular weights of the copolymers were determined by viscometry or osmometry. The following viscosity-molecular weight relationship was used²¹:

$$[\eta] = 44 \times 10^{-5} \times \bar{M}_v^{0.65}$$

Intrinsic viscosities were measured at 25°C in a toluene solution. The molecular weights of these copolymers are obviously approximate values since the preceding relation was given for pure polystyrene. Number average molecular weights of the copolymers were measured by means of a membrane osmometer, at 35°C, in toluene.

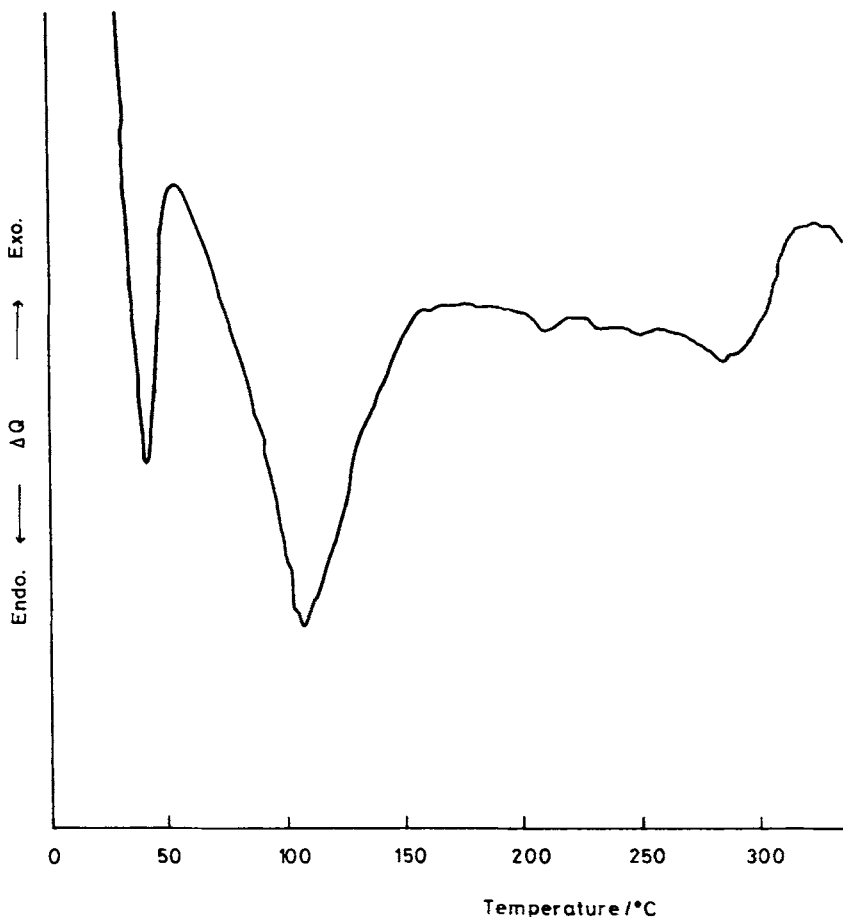


Fig. 2. DSC thermogram of copolymer 11 (21.15 mg of sample, 34.0% PEG-20,000).

Number average and weight average molecular weights of a few samples are determined from the GPC measurements.

Intermediates and products were characterized by IR spectroscopy after each step.

DSC thermograms were conducted on polymer samples of about 21 mg.

Copolymers were molded at 125°C whereas reference polystyrene was molded at 155°C at a pressure of 6.9 MN/m² for all mechanical testings.

RESULTS AND DISCUSSION

Twelve copolymers of styrene and poly(ethylene oxide) were synthesized from the six peroxy-carbamates already described. Table II contains the conditions chosen for the preparation of copolymers. In this table, PEG-4000 was used for the first six samples and PEG-20,000 for the remaining polymers. The weight percentage of poly(ethylene oxide) (PEO) incorporated into the polymeric product ranged from 4.0 to 36.5% (run 1 and 12). As the proportion of

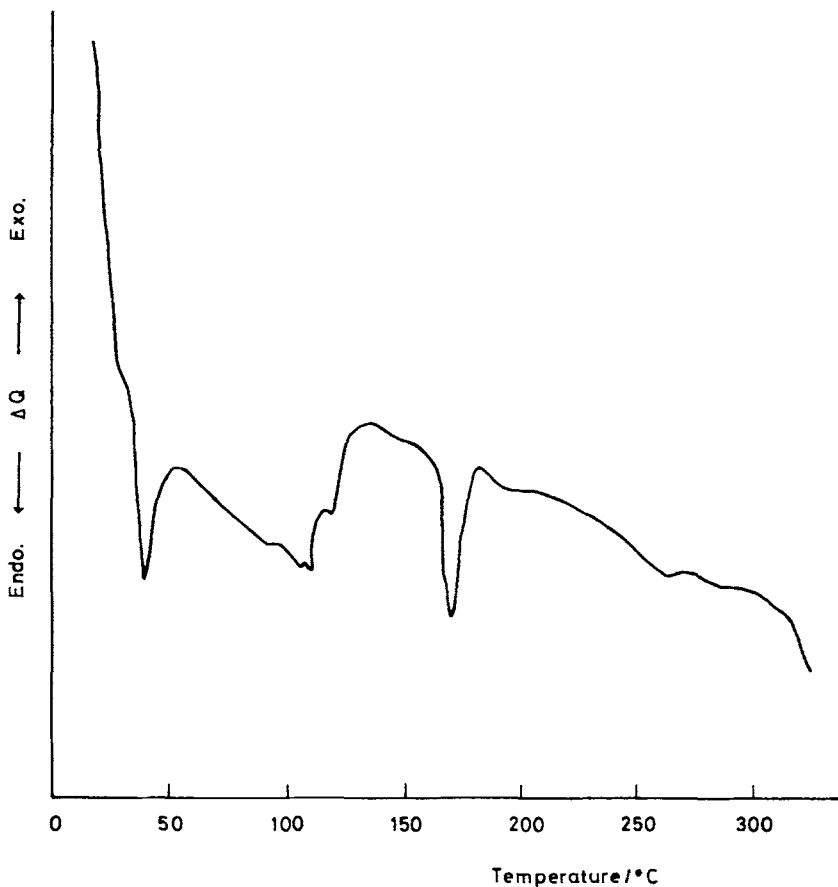


Fig. 3. DSC thermogram of copolymer 6 (21.17 mg of sample, 30.8% PEG-4000).

PEO incorporated into the polymeric material increases, the overall conversion of styrene to polymer and the molecular weights of the final products decrease for copolymers based on both PEG-4000 and PEG-20,000.

Figure 1 illustrates representative GPC results for copolymers 3 and 10.

Number and weight average molecular weights were calculated from this GPC results as 2.23×10^5 and 5.31×10^5 for copolymer 3; 1.75×10^5 and 3.62×10^5 for copolymer 10, respectively. Molecular weight distributions were found to be 2.4 for copolymer 3 and 2.7 for copolymer 10. These results are comparable to the viscometric molecular weight results of the samples 2.16×10^5 and 2.04×10^5 for copolymers 3 and 10, respectively.

Temperature programming was used for copolymerization except for copolymers 3 and 7. For this purpose, polymerization was started at 80°C and ended at 93°C . Theoretical considerations underlying this temperature programming procedure have been given previously.^{11,13,22} The aim is to obtain a size distribution of vinyl blocks having no unreacted peroxidic group left embedded in the copolymer. This 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 consumption of the vinyl monomer.

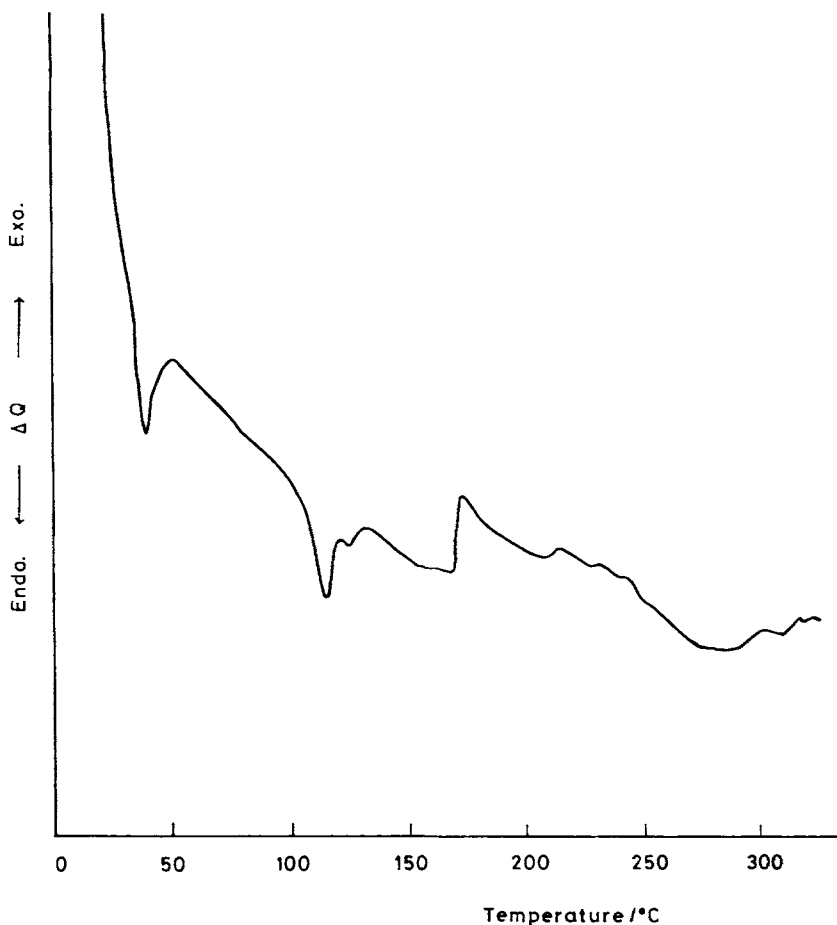


Fig. 4. DSC thermogram of copolymer 5 (21.08 mg of sample, 25.7% PEG-4000).

In this work, the upper temperature for incorporation of polystyrene blocks was chosen to be 93°C because the rate of decomposition of peroxy-carbamates similar to that used in this work is approximately equal to the $(1/e)$ life of styrene consumption at this temperature.^{11,13}

In the infrared spectra of the reactants and intermediates, the peak at 3520 and 3590 cm^{-1} are due to the H-bonded OH groups. These OH absorption peaks disappeared at the end of capping reaction with diisocyanate. The peak at 2280 cm^{-1} is due to the stretching vibration of —NCO , and it is the principal absorption peak for isocyanate groups (compound I). In the second reaction step disappearance of this peak indicates the formation of dicarbamate (compound II). In the infrared spectra of the copolymers, peaks around 3440 cm^{-1} were observed in all runs. This absorption is due to the —N— stretching in

$$\begin{array}{c} | \\ \text{—N—} \\ | \\ \text{H} \end{array}$$

the —N—C— group of the peroxy-carbamate. This absorption peak in the

$$\begin{array}{c} | \quad || \\ \text{H} \quad \text{O} \end{array}$$

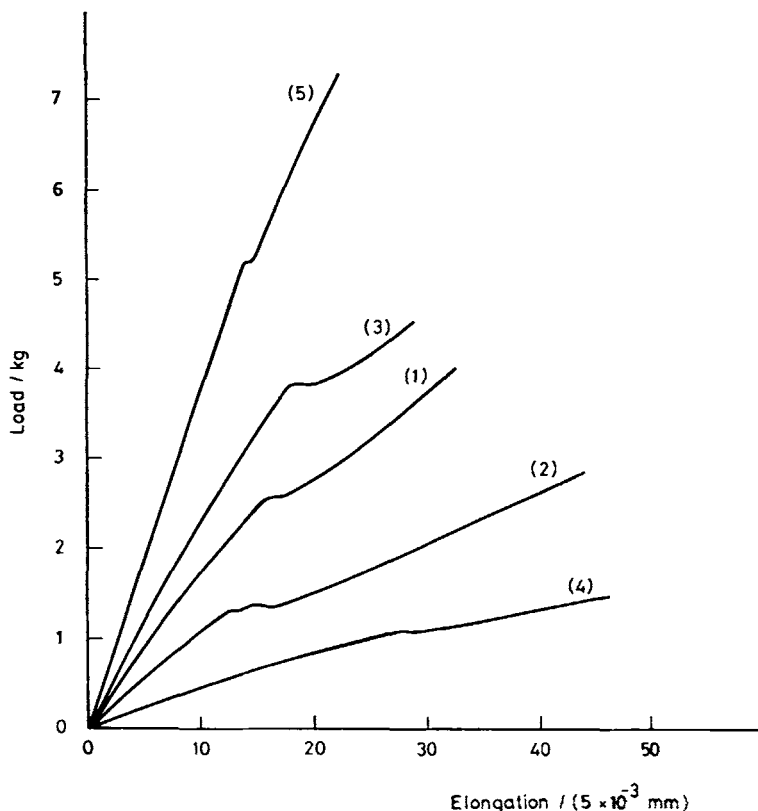


Fig. 5. Stress-strain curves of the copolymers: (1) Copolymer 2, 8.6% PEG-4000; (2) copolymer 6, 30.8% PEG-4000; (3) copolymer 8, 7.6% PEG-20,000; (4) copolymer 11, 34.0% PEG-20,000; (5) pure PS.

spectrum indicates the incorporation of the peroxy-carbamate into the copolymers, which provides evidence for block copolymer formation.

It may be anticipated that polymerization in such a system would inevitably result in the formation of polystyrene homopolymer. It should be mentioned that evidence against homopolymer formation was obtained when a polymeric peroxy-carbamate was used as the initiator in an earlier study.¹³ Since the termination reaction in styrene polymerization usually occurs by combination of two radicals, the percentage of homopolymer may be close to 25% of the total product obtained in this work.

In these block copolymers, since each of the two different segments retains its own properties, in DSC studies above 0°C, the melting point (T_m) of PEO and the glass transition temperature (T_g) of polystyrene (PS) should be observed. This system exhibits unusual characteristics as their crystalline and amorphous components exhibit transition temperatures such as $T_m < T_g$.²³ The length of the blocks and the structure of copolymers may shift the locations of T_g and T_m . Figures 2-4 represent the DSC thermograms of typical copolymeric samples. These three scans are almost identical.

The crystalline melting point of poly(ethylene oxide) blocks decreases from its original value (60°C) to about 40°C as it has been observed in an earlier

TABLE III
Mechanical Characteristics of Copolymers

Copolymer number	Styrene weight (%)	Elongation (%)	Tensile strength MN/m ²	Ultimate tensile strength MN/m ²	Young's modulus MN/m ²	Hardness, Shore D
1	96.0	2.89	6.81	18.3	980	81
2	91.4	2.95	6.53	17.1	810	80
3	87.8	3.16	6.30	16.5	780	—
4	86.4	3.51	6.26	15.0	710	78
5	74.3	3.56	6.05	12.6	630	71
6	69.2	3.85	5.70	12.0	510	70
7	95.5	2.46	21.0	25.8	1270	83
8	92.4	2.56	16.1	19.1	1030	81
9	84.6	2.59	7.19	14.6	750	70
10	84.0	2.65	6.40	12.5	670	—
11	66.0	4.11	4.63	6.25	200	—
PS Homopolymer	100.0	2.00	22.1	30.8	1670	—

morphological study of crystalline multiblock copolymer of styrene-ethylene oxide components.²³ It is known that the degree of crystallinity varies with copolymer composition. As it was anticipated, crystallization of the PEO blocks becomes more difficult as the PS content increases.²⁴ If the PS content exceeds about 80%, an amorphous copolymeric material is obtained. DSC thermograms of these copolymers (5, 6, and 11) were obtained with the same amount materials. Figures 2-4 show that as the PS content increases, the percent crystallinity of the PEO component decreases, as it can be seen by comparing the melting peak areas around 40°C.

The glass transition temperature of polystyrene blocks increased to 105-115°C. It was reported that at temperatures above T_g values, two transition zones can be distinguished by isothermal measurements.^{25,26} An increase by about 10°C of T_g is observed in elastic modulus-temperature diagrams of block copolymers with the same components but prepared with different diisocyanates.¹² The same behavior is reported for polyester-polystyrene block copolymers.²⁷

The peak observed at about 170°C (Fig. 3) is related to the urethane residue of the block copolymer. Similar peaks were also reported in DSC diagrams of polyurethane block copolymers.^{28,29}

Typical stress-strain curves obtained from the Tensilon are shown in Figure 5. It will be seen from the curves that, as the PS contents of the samples are lowered, Young's modulus and yield values decrease; in the meanwhile, elongations increase and yield plateaus extend.

Tensile strength, ultimate tensile strength, percent elongation, and Young's modulus were calculated from the stress-strain curves for the block copolymer samples and for a reference polystyrene. The average values of these mechanical properties are given in Table III. It is observed from this table that the elongation at break for the PS reference is 2.00%; the elongations of copolymers are in the range of 2.46 and 4.11%. Tensile strength, ultimate tensile strength, and

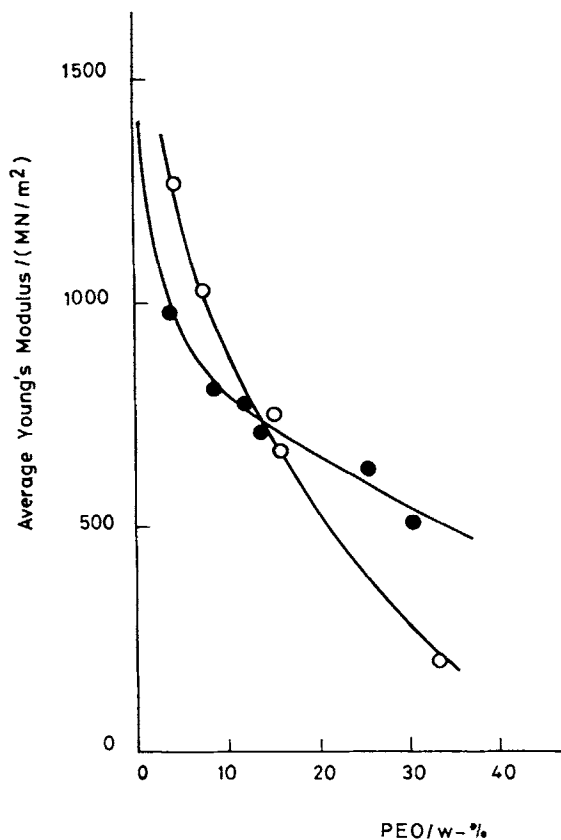


Fig. 6. Average Young's modulus vs. PEO content: ● Copolymers containing PEG-4000; ○ copolymers containing PEG-20,000.

Young's modulus of copolymeric samples also decrease, when the PS contents of the samples prepared by using either PEG-4000 or PEG-20,000 decrease.

The average Young's modulus (\bar{E}) of the copolymeric samples were plotted against weight percent of the soft component in Figure 6. The values of Young's modulus exhibit a tendency to decrease, for both PEO constituents used in this work. The lower and the upper limiting values of \bar{E} are 200 and 1270 MN/m², respectively. The range of these values are comparable with the values reported for styrene-isoprene-styrene triblock films.³⁰

The hardness of copolymers (Table III) were found between 83-70 Shore D depending on the molecular weight and on the PS content of the copolymers. These values are comparable with the values of urethane elastomers reported in the literature.³¹

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