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Ultrasonic Modification of Polymers. I. Degradations of Polystyrene in the Presence of Various Poly(alkyl Methacrylates)

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ABSTRACT

Ultrasonic (70 W, 20 kHz) degradations of polystyrene (PS) have been carried out with various poly(alkyl methacrylates) (PRMA) for periods of 3 h at 27°C in toluene (2.0 to 5.0% solutions). The isolation of sequence copolymers thus prepared from their associated homopolymers was achieved by employing selective solvents (solvent for one homopolymer but a precipitant for the second homopolymer in the mixture). The recovered products were analyzed by gel permeation chromatography (GPC), infrared spectroscopy (IR), and viscometry. These analyses showed that when the substituents in PRMA were methyl, ethyl, isopropyl, n-butyl, isobutyl, or phenyl, sequence copolymers with segments from PS as well as from poly(alkyl methacrylate) were obtained. However, when the substituents on PRMA were hexyl, isodecyl, lauryl, hexadecyl, octadecyl or isobornyl there were no sequence copolymers formed. The decrease in the intrinsic viscosity of the recovered homopolymers and shifts of their GPC chromatograms toward the low molecular weight end suggest that on sonification PRMA samples having bulkier substituents do degrade and yield radicals which, however, do not recombine with those from polystyrene. Furthermore, ultrasonic degradation of polystyrene is found to be dependent on the chain stiffness of the poly(alkyl methacrylates).

INTRODUCTION

When an ultrasonic field is applied to a polymer solution, cavitation [1-6] may result and a small fraction of energy is used in shearing molecules to yield homolytic cleavage [7-13]. If this can be made to occur in the presence of (1) a polymer and a polymerizable vinyl monomer [23-27] or (2) two homopolymers [28-33], the reactions may lead to the formation of block copolymers which would carry segments from the polymer and the added monomer (Case 1) or segments from both homopolymers (Case 2). The only requirement for making block copolymers with ultrasonic polymerization is that the two polymers or the polymer and the vinyl monomer should be soluble in a common solvent.

These chemically bonded polymers exhibit properties which are generally superior to those obtained by physical blends of the same two polymers. A unique development resulting from block copolymer technology is the concept of thermoplastic elastomeric behavior [34]. Block copolymers carrying a minor fraction of hard segments (e.g., polystyrene) and a major fraction of soft segments [e.g., poly(methyl methacrylate)] show the best thermoplastic elastomeric behavior because the hard segments associate to form morphological domains that serve as physical cross-links and reinforcement sites. Most of the work cited in the literature on ultrasonic block copolymerization has been restricted to polystyrene-poly(methyl methacrylate). With a view to extending these studies, block copolymerization of polystyrene has been attempted with other poly(alkyl methacrylates).

The separation of block copolymers from homopolymers was achieved by selective solvent/nonsolvent pair combination as described in the literature [26]. For example, in a mixture of polystyrene, poly(methyl methacrylate), and a block copolymer of polystyrene-poly(methyl methacrylate), we used (1) extraction with acetonitrile, which is selective solvent for poly(methyl methacrylate) but a precipitant for polystyrene, and (2) extraction with cyclohexane, which is a moderate solvent for polystyrene but a nonsolvent for poly(methyl methacrylate), leaves behind an insoluble product which carries components from polystyrene as well as poly(methyl methacrylate) and may possibly be a block copolymer. As in the ultrasonic block copolymerizations, the insoluble product may have little order of sequences as compred to the highly ordered block copolymers poly(styrene-b-methyl methacrylate). The former has been presented here as polystyrene-poly(methyl methacrylate). These polymers have sometimes been referred to as scrambled copolymers due to the unpredictable nature of polymer-polymer recombination processes.

EXPERIMENTAL

Materials

Samples of polystyrene (Pressure Chemical Co.) [poly(methyl methacrylate), poly(ethyl methacrylate), poly(isopropyl methacrylate), poly(phenyl methacrylate), poly(benzyl methacrylate), poly(lauryl methacrylate), poly(isobornyl methacrylate), poly(octadecyl methacrylate)] (scientific polymer), [poly(n-butyl methacrylate), poly(isobutyl methacrylate), poly(hexyl methacrylate, poly(isodecyl methacrylate), and poly(cyclohexyl methacrylate)] (Aldrich Chemical Co.) were used as received.

Degradation Procedure

Ultrasonic degradations of polymer solutions were carried out in a batch reactor (10 cm long, 5 cm diameter, 200 mL capacity) equipped with water jackets to maintain a 2°C temperature measured with a Nl-Cr alloy probe and a Comark digital thermometer (Fig. 1). Prior to subjecting the polymer solutions to ultrasonic treatments, they were purged with nitrogen for a period of 30 min. The sealed aluminum reactor was screwed onto a threaded nodal point on a 1.25 cm diameter disruptor horn (Heat Systems Model 375A with a nominal frequency of 20 kHz) where attachment produces no damping. Ultrasonic intensity of 70 W was adjusted using the calibration curve of meter reading, power control setting, and power output in watts provided by the manufacturer. After sonicating the polymer solution for the desired period of time, it was transferred to a 1-L beaker and the solvent was removed by evaporation. The dried products were subjected to fractionation for the removal of homopolymers by using different solvent/nonsolvent systems. Solvent pairs were chosen in such a way that each solvent dissolved only one of the polymers and acted as a nonsolvent for the other. All products (homopolymers as well as block copolymers) recovered after fractionation were analyzed by Infrared (IR), gel permeation chromatography (GPC) and viscometry.

Characterization of Polymers

IR Analyses

The IR spectra of polymers were recorded from thin films (prepared on KBr disks) on a Beckman Spectrophotometer Model 4250.

Viscosity Calculations

Calculations of the intrinsic viscosity of sonicated polymers and block copolymers were carried in THF by making use of the flow

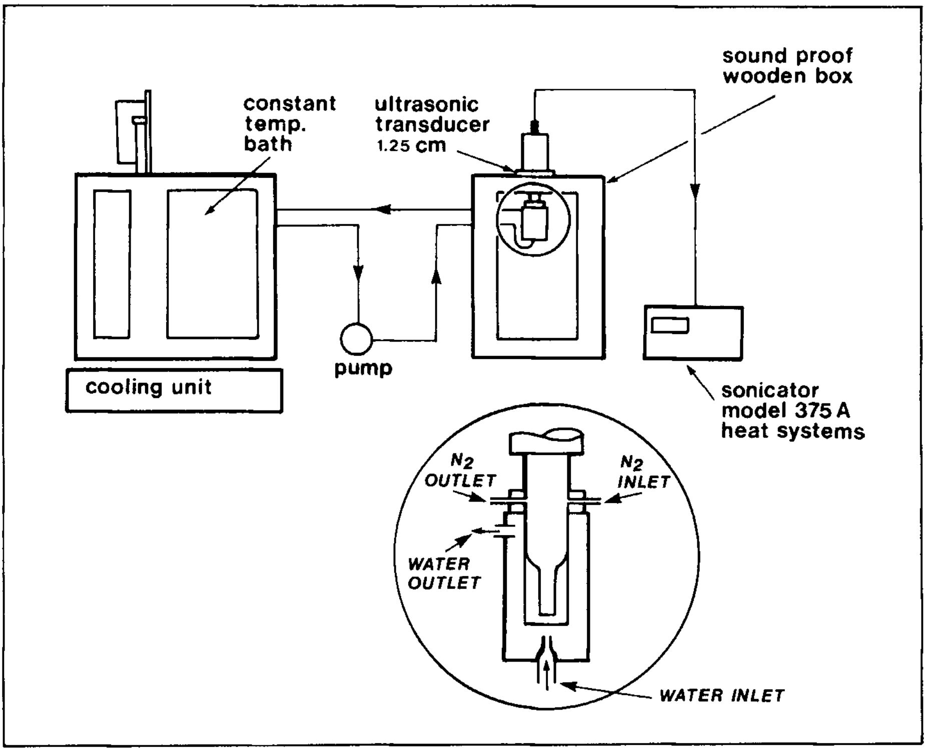


FIG. 1. Schematic diagram for ultrasonic block copolymerization.

time measurement data obtained with Ubbelohde viscometers at 25°C for at least three concentrations. Knowing the flow time of the solvent THF and the solutions, the computation of the intrinsic viscosity $[\eta]$ is carried out with

$$[\eta] = \lim_{c \to 0} \eta_{sp}/c \tag{1}$$

where

$$\eta_{sp}/c = \left(\frac{\text{flow time of solution}}{\text{flow time of solvent}} - 1 \right)$$

Huggins coefficient k_H is related to $[\eta]$ by

$$(\eta_{sp}/c) = [\eta] + k_H[\eta]^2 c \tag{2}$$

Viscosity measurements of the untreated homopolymers were also measured in other solvents for which the Mark-Houwink constants K and a are reported in the literature.

Gel Permeation Chromatographic Analyses

Molecular weight distributions of polymers were carried out with a Waters Associates GPC (equipped with a high pressure solvent delivery system, Model 6000 A), an ultraviolet absorbance detector (Model 440), and a differential refractometer (Model R401) operated at 25°C. The separating system consisted of four μ-styragel columns connected in series, each packed with cross-linked polystyrene gel having (by the Waters method) pore sizes of 500, 1×10^3, 1×10^4, and 1×10^5 Å, respectively. The flow of the solvent tetrahydrofuran was maintained at 1 mL/min while the concentration of the polymer solution was limited to 0.2% in order to render "concentration effects" negligible on the peak position in the chromatograms. Calibration of the instrument was performed with standard polystyrene samples. Calibration curve relating elution volume V_e and molecular weight M yielded the relation

$$\ln M = 24.03 - 0.44V_e \tag{3}$$

Viscosity-average molecular weights $\overline{M}_v$ of three poly(methyl methacrylate) samples of different molecular weights were calculated from the intrinsic viscosity data obtained in toluene [35]. Making use of the GPC and viscosity data, elution volume V_e was related to molecular weight M by

$$\ln M = 27.54 - 0.56V_e \tag{4}$$

Similarly, assuming a constant slope of -0.56 in conjunction with viscosity [36] and GPC data, V_e and M for various other poly(alkyl methacrylates), viz., [poly(ethyl methacrylate) and poly(lauryl methacrylate), Eq. 5], [poly(n-butyl methacrylate), poly(cyclohexyl methacrylate), and poly(hexyl methacrylate), Eq. 6], [poly(isobutyl methacrylate), poly(isobornyl methacrylate), poly(isopropyl methacrylate), and poly(isodecyl methacrylate) Eq. 7], [poly(octadecyl methacrylate) and poly(hexadecyl methacrylate), Eq. 8], and [poly(phenyl methacrylate) and poly(benzyl methacrylate) Eq. 9], are as follows:

$$\ln M = 27.22 - 0.56V_e \tag{5}$$

$$\ln M = 27.36 - 0.56V_e \tag{6}$$

$$\ln M = 27.78 - 0.56V_e \tag{7}$$

$$\ln M = 28.72 - 0.56V_e \tag{8}$$

$$\ln M = 28.43 - 0.56V_e \tag{9}$$

With the help of Eqs. (3) to (9), weight-average $\overline{M}_w$ and number-average $\overline{M}_n$ molecular weights of the homopolymers were computed from the uncorrected GPC chromatograms using the summation method [37]. The molecular weights of the copolymers were assumed to be the weighted averages of the log molecular weights of the homopolymers of the constituent comonomers. For example, in the case of a block copolymer of polystyrene and poly(methyl methacrylate) (PMMA), $\overline{M}_w$ and $\overline{M}_n$ values were computed using polystyrene calibration curve ($\overline{M}_{w(PS)}$, $\overline{M}_{n(PS)}$ as well as with that of PMMA ($\overline{M}_{w(PMMA)}$, $\overline{M}_{n(PMMA)}$). Knowing the composition of the block copolymer, molecular weights were then computed as follows:

$$\log \overline{M}_w = X_{PS} \log \overline{M}_{w(PS)} + X_{PMMA} \log \overline{M}_{w(PMMA)} \tag{10}$$

$$\log \overline{M}_n = \frac{1}{X_{PS}} \log \overline{M}_{n(PS)} + \frac{1}{X_{PMMA}} \log \overline{M}_{n(PMMA)} \tag{11}$$

where $\overline{M}_w$ and $\overline{M}_n$ are the molecular weights of the block copolymer, and X_{PS} and X_{PMMA} are the weight fractions of PS and PMMA, respectively, in the block copolymer ($X_{PS} + X_{PMMA} = 1$). A similar approach has been suggested by Runyon et al. [38]. Copolymer molecular weights have not been computed from combined GPC-intrinsic viscosity data using the universal calibration curve as suggested by Ho-Duc and Prud'homme [39] because the work of Dondos et al. [40] has shown that for block copolymers (in good solvents), the weighted average method is acceptable.

RESULTS AND DISCUSSION

Polystyrene (PS)-Poly(methyl Methacrylate) (PMMA)

2.0 g PS ($\overline{M}_w = 1.8 \times 10^6$, $\overline{M}_w/\overline{M}_n = 1.45$, $[\eta] = 4.8$ dL/g) and 4.4 g PMMA ($\overline{M}_w = 6.65 \times 10^5$, $\overline{M}_w/\overline{M}_n = 4.35$, $[\eta] = 1.06$ dL/g, $k_H = 0.36$) were dissolved in 175 mL of toluene and purged with dry nitrogen for 30 min prior to subjecting the solution to ultrasonic treatment at 27°C for 180 min. The resulting product was dried by evaporating the solvent at room temperature. A mixture [of methyl ethyl ketone (300 mL) and isopropanol (700 mL)] which is a precipitant for PS but a good solvent of PMMA was added to the dry polymer product to recover 4.0 g of PMMA homopolymer ($[\eta] = 0.96$ dL/g, $k_H = 0.32$, $\overline{M}_w = 5.1 \times 10^5$, $\overline{M}_w/\overline{M}_n = 1.62$). Subsequent treatment with 500 mL of cyclohexane which is a precipitant for PMMA but a solvent for PS removed 700 mg of PS homopolymer leaving behind 1.7 g of the insoluble block copolymer (PS-PMMA). GPC chromatograms of untreated homopolymers, unspent homopolymers recovered after ultrasonic treatment, and the block copolymer PS-PMMA are shown in Fig. 2, and the IR spectrum of the block copolymer PS-PMMA is presented in Fig. 3. Characteristic peaks of PS between 3000 and 3100 cm^{-1} and those of PMMA at 1760 cm^{-1} indicate that a block copolymer has been formed. From knowledge of the weight of the starting and the end products, the composition of the block copolymer was found to be 77% PS and 23% PMMA (Table 1). Molecular weights ($\overline{M}_w = 5.9 \times 10^5$ and $\overline{M}_n = 3.45 \times 10^5$) of this block copolymer were calculated using the weighted average method, and a value of $\overline{M}_w/\overline{M}_n = 1.7$ suggests that narrow polydispersity block copolymers can be prepared with ultrasound.

Polystyrene (PS)-Poly(ethyl Methacrylate) (PEMA)

2.0 g PS ($\overline{M}_w = 1.8 \times 10^6$, $\overline{M}_w/\overline{M}_n = 1.45$, $[\eta] = 4.8$ dL/g) and 2.0 g PEMA ($\overline{M}_w = 3.46 \times 10^5$, $\overline{M}_w/\overline{M}_n = 3.0$, $[\eta] = 0.77$ dL/g, $k_H = 0.17$) were dissolved in 175 mL of toluene, purged with dry nitrogen for 30 min, and sonicated at 27°C for 180 min. Evaporation of solvent yielded a mixture of dry polymers from which 1.2 g of PEMA homopolymer ($\overline{M}_w = 2.84 \times 10^5$, $\overline{M}_w/\overline{M}_n = 3.9$, $[\eta] = 0.76$ dL/g, $k_H = 0.31$) was recovered using a mixture of methyl ethyl ketone (200 mL) and isopropanol (800 mL) while 200 mg of PS homopolymer ($\overline{M}_w = 1.87 \times 10^5$, $\overline{M}_w/\overline{M}_n = 2.1$, $[\eta] = 0.76$ dL/g, $k_H = 0.17$) was obtained with

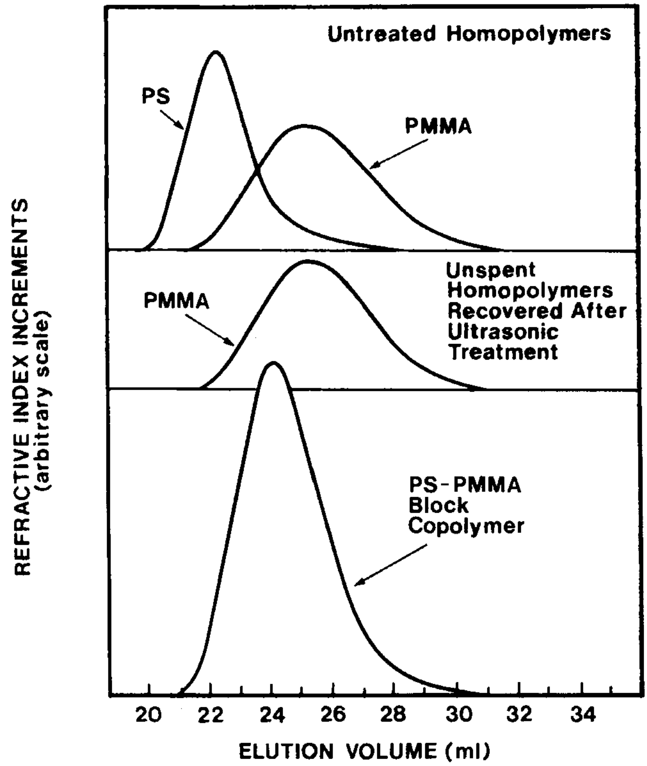


FIG. 2. GPC chromatograms of the starting materials (untreated homopolymers), polymers recovered with 1st and 2nd extractions with selective solvents (unspent homopolymers recovered after ultrasonic treatment) and the insoluble product (block copolymer) in a reaction involving PS and PMMA.

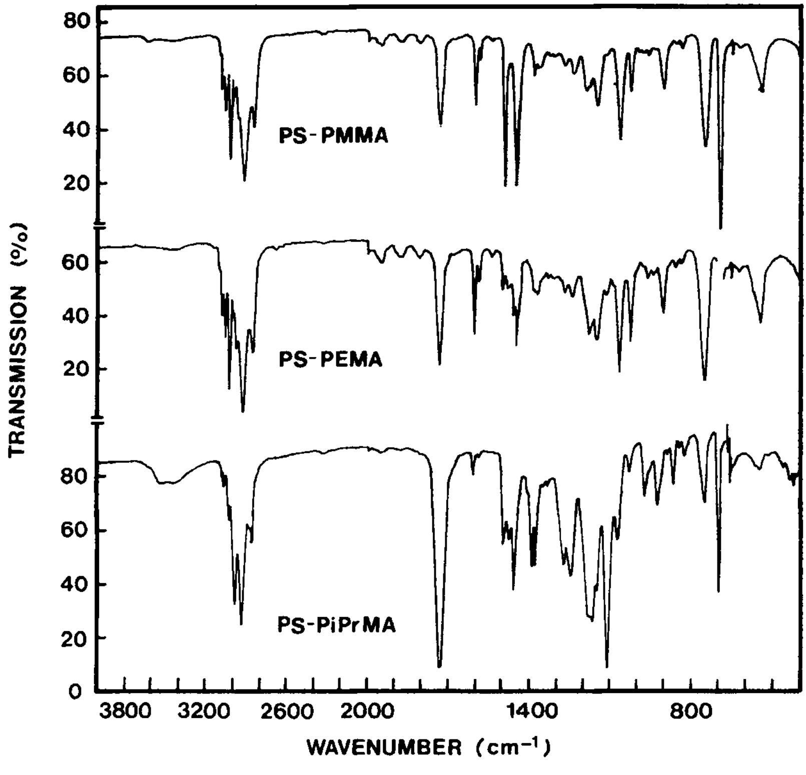


FIG. 3. IR spectra of the insoluble products recovered in the block copolymerizations of PS with PMMA, PEMA, and PIPrMA.

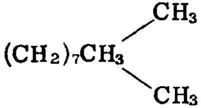
TABLE 1. Characteristics of Block Copolymers of PS with Poly(alkyl Methacrylates) (PRMA)

No.	Substituent R	Composition (%) PS	PRMA	Molecular weights $\overline{M}_w$ (GPC) × 10^{-3}	$\overline{M}_n$ (GPC) × 10^{-3}	$\overline{M}_w/\overline{M}_n$	$[\eta]^a$ (dL/g)	Huggins coefficient (k_H)
X-55	Methyl	77	23	590	345	1.7	1.44	0.36
X-64	Ethyl	70	30	550	289	1.9	1.74	0.17
X-43	Isopropyl	45	55	585	163	3.6	0.81	0.53
X-52	n-Butyl	67	33	470	215	2.2	1.01	0.50
X-59	Isobutyl	77	23	1100	425	2.6	2.66	0.38
X-44	Phenyl	60	40	375	100	3.7	0.74	0.53
X-56[b]	Cyclohexyl	60	40	400	100	4.0	0.80	0.62
X-65[b]	Benzyl	55	45	359	52	6.9	0.94	0.45
X-66[b]	Isodecyl	86	14	500	220	2.2	1.25	0.46

[a] In THF at 25°C.

[b] May only be a blend of two homopolymers.

TABLE 2. Ultrasonic Solution Degradation of PS in the Presence of Various Poly(alkyl Methacrylates) (PRMA) for a Period of 3 h at 27° C

			Nondegraded PS				Degraded PS			
No.	Substituent	Structure	$[\eta]^a$ (dL/g)	$\overline{M}_w \times 10^{-3}$ (GPC)	$\overline{M}_n \times 10^{-3}$ (GPC)	$\frac{\overline{M}_w}{\overline{M}_n}$	$[\eta]^a$ (dL/g)	$\overline{M}_w \times 10^{-3}$ (GPC)	$\overline{M}_n \times 10^{-3}$ (GPC)	$\frac{\overline{M}_w}{\overline{M}_n}$
X-39	Hexyl	$-(CH_2)_5CH_3$	4.8	1800	1240	1.45	1.5	450	295	1.5
X-66	Isodecyl	 $\overset{CH_3}{\underset{CH_3}{(CH_2)_7CH_3}}$	4.8	1800	1240	1.45	1.25	500	220	2.2
X-38	Hexadecyl	$-(CH_2)_{15}CH_3$	4.8	1800	1240	1.45	1.33	350	240	1.45
X-31	Octadecyl	$-(CH_2)_{17}CH_3$	4.8	1800	1240	1.45	2.55	715	470	1.5
X-40	Lauryl	$-(CH_2)_{11}CH_3$	2.25	900	700	1.3	1.15	335	217	1.6
X-42	Isobornyl	$C_{10}H_{17}$	2.25	900	700	1.3	1.24	380	280	1.35

[a] In THF at 25° C.

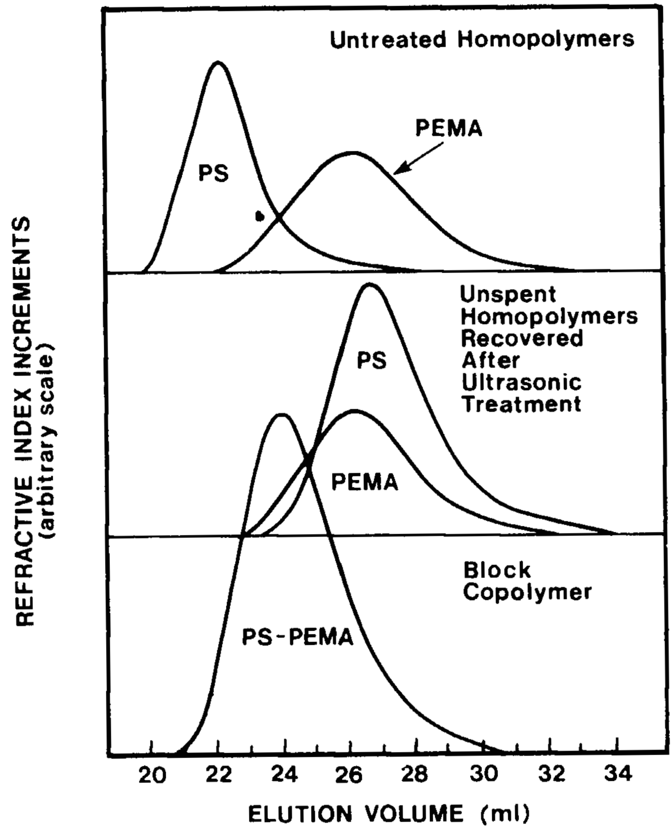


FIG. 4. GPC chromatograms of polymers involved in the block copolymerization of PS and PEMA.

cyclohexane, leaving behind 2.6 g of block copolymer (see Fig. 3) PS-PEMA (70% PS, 30% PEMA) with $\overline{M}_w = 5.5 \times 10^5$, $\overline{M}_n = 2.89 \times 10^5$, $[\eta] = 1.74$ dL/g, and $k_H = 0.17$. These molecular weights were computed from the GPC chromatograms shown in Fig. 4.

Polystyrene (PS)-Poly(isopropyl Methacrylate) (PiPrMA)

2.0 g PS ($\overline{M}_w = 9.0 \times 10^5$, $\overline{M}_w/\overline{M}_n = 1.3$, $[\eta] = 2.25$ dL/g) and 4.2 g PiPrMA ($\overline{M}_w = 8.0 \times 10^5$, $\overline{M}_w/\overline{M}_n = 10.5$, $[\eta] = 1.22$ dL/g, $k_H = 0.11$)

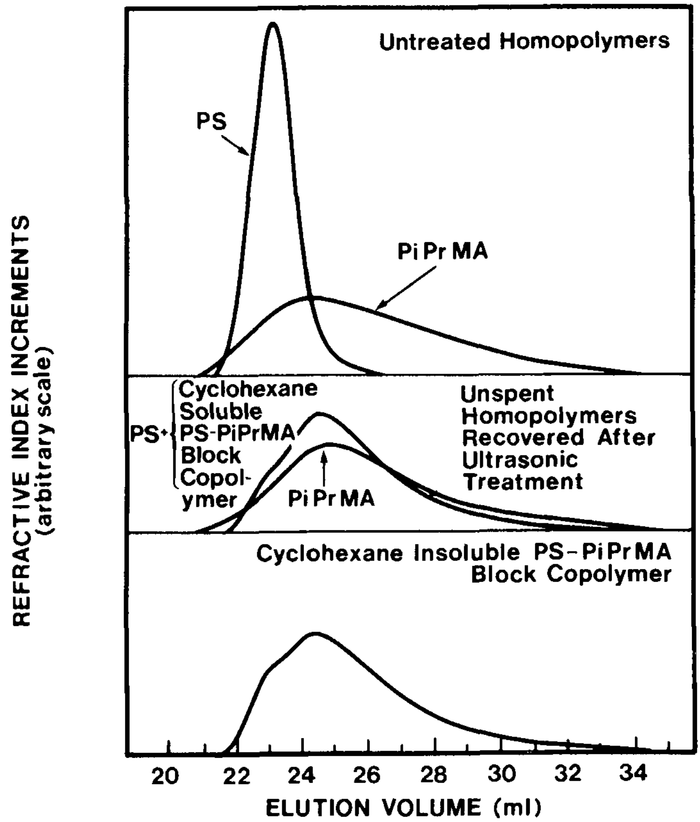


FIG. 5. GPC chromatograms of polymers involved in the block copolymerization of PS and PIPrMA.

were dissolved in toluene, purged with nitrogen for 30 min, and sonicated at 27°C for 210 min. Evaporation of solvent yielded a mixture of dry polymers from which 250 mg PS ($\overline{M}_w = 3.85 \times 10^5$, $\overline{M}_n = 1.7 \times 10^5$, $[\eta] = 0.74$ dL/g, $k_H = 0.0$) was obtained with cyclohexanol, leaving behind 4.0 g of block copolymer PS-PiPrMA (Fig. 3) (45% PS, 55% PiPrMA) with $\overline{M}_w = 5.85 \times 10^5$, $\overline{M}_n = 1.63 \times 10^5$, $[\eta] = 0.81$ dL/g, and $k_H = 0.53$. Cyclohexane, acetonitrile, isopropanol, methyl isobutyl ketone and (methyl isobutyl ketone + acetone) are nonsolvents for PiPrMA. These molecular weights were computed from the GPC chromatograms shown in Fig. 5.

Polystyrene (PS)-Poly(n-butyl methacrylate) (PnBuMA)

3.75 g PS ($\bar{M}_w = 1.8 \times 10^6$, $\bar{M}_w/\bar{M}_n = 1.45$, $[\eta] = 4.8$ dL/g, and 4.0 g PnBuMA ($\bar{M}_w = 3.2 \times 10^5$, $\bar{M}_w/\bar{M}_n = 3.75$, $[\eta] = 0.4$ dL/g, $k_H = 0.52$) were dissolved in 350 mL toluene, purged with nitrogen for 30 min, and sonicated (in two batches) for 180 min each. Evaporation of solvent yielded a mixture of dry polymers from which 2.55 g PnBuMA ($\bar{M}_w = 3.1 \times 10^5$, $\bar{M}_w/\bar{M}_n = 3.5$, $[\eta] = 0.60$ dL/g, $k_H = 0.31$) was recovered using isopropanol while 250 mg PS ($\bar{M}_w = 3.6 \times 10^5$, $\bar{M}_w/\bar{M}_n = 1.9$, $[\eta] = 1.15$ dL/g, $k_H = 0.19$) was obtained with cyclohexane, leaving behind 5.0 g of block copolymer PS-PnBuMA (67% PS, 33% PnBuMA) with $\bar{M}_w = 4.7 \times 10^5$, $\bar{M}_n = 2.15 \times 10^5$, $[\eta] = 1.01$ dL/g, and $k_H = 0.50$. These molecular weights were computed from the GPC chromatograms shown in Fig. 6 while the presence of both components of the block copolymer is confirmed by the IR spectrum presented in Fig. 7.

In Fig. 8 are presented two electron micrographs of the block copolymer PS-PnBuMA taken with a Phillips Model 400 at 100 kV of applied voltage. A drop of polymer solution (1%) in THF was evaporated directly on the carbon-coated grid to form a thin film for electron microscopic analyses. Spherical domains ranging from 90 to 160 nm in size appear light in color and dispersed in a dark continuous matrix. Based on composition, we postulate the spherical domains to be PnBuMA segments dispersed in a continuum of styrene segments. It would appear that though it is relatively easy to prepare block copolymers with ultrasound, their morphological behavior falls in between that of the microscale morphology of the anionically prepared block copolymers and the macroscale dimensions of incompatible blends.

Polystyrene (PS)-Poly(isobutyl Methacrylate) (PiBuMA)

2.0 g PS ($\bar{M}_w = 1.8 \times 10^6$, $\bar{M}_w/\bar{M}_n = 1.45$, $[\eta] = 4.8$ dL/g) and 7.0 g PiBuMA ($\bar{M}_w = 5.9 \times 10^5$, $\bar{M}_w/\bar{M}_n = 2.85$, $[\eta] = 0.64$ dL/g, $k_H = 0.4$) were dissolved in 175 mL of toluene purged with nitrogen, and sonicated for 180 min at 27°C. Evaporation of the solvent yielded a mixture of dry polymers from which 6.4 g PiBuMA ($\bar{M}_w = 4.62 \times 10^5$, $\bar{M}_n = 1.63 \times 10^5$, $[\eta] = 0.66$ dL/g, $k_H = 0.48$) was recovered with acetone while subsequent treatment with cyclohexane yielded only

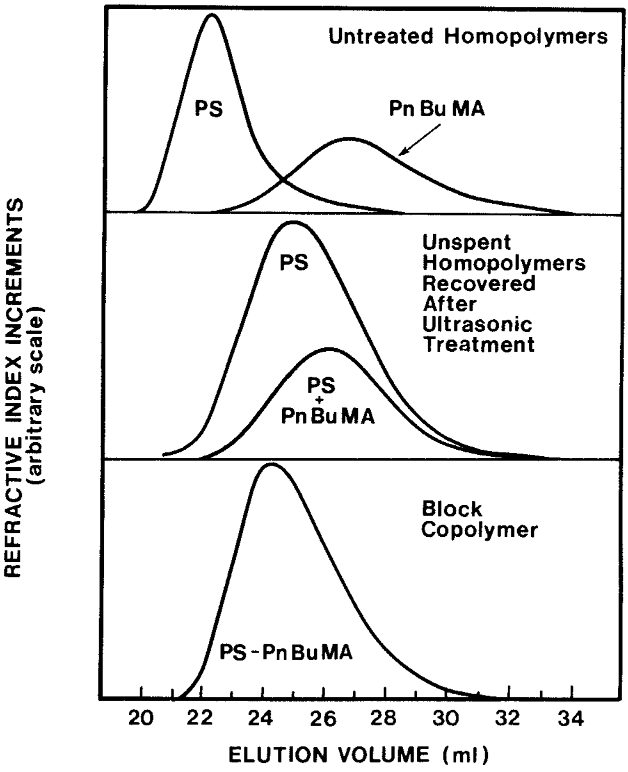


FIG. 6. GPC chromatograms of polymers involved in the block copolymerization of PS and PnBuMA.

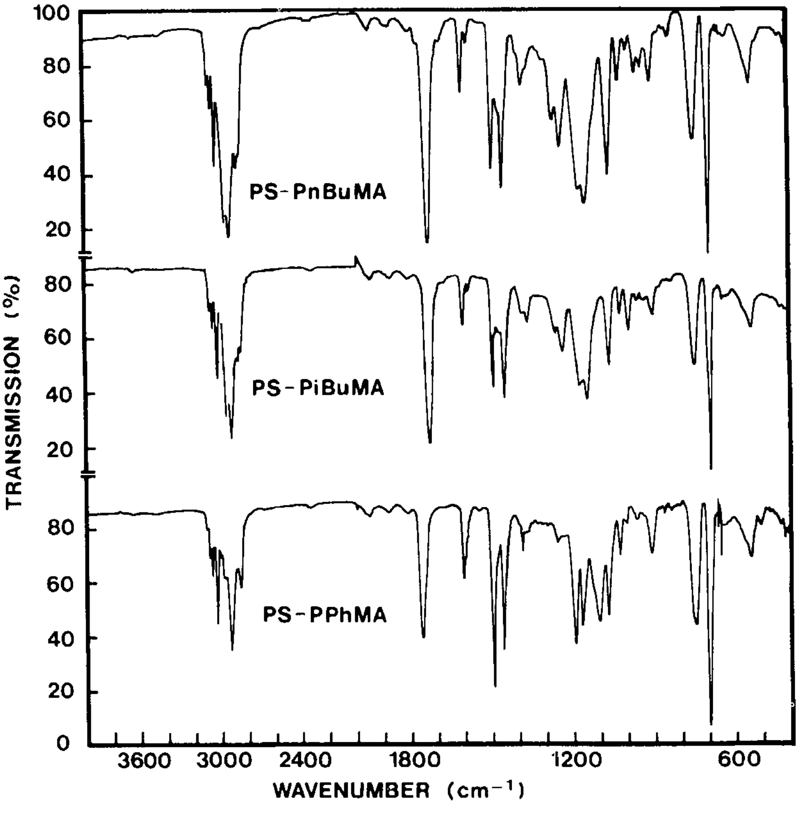


FIG. 7. IR spectra of the insoluble products recovered in the block copolymerization of PS with PnBuMA, PiBuMA, and PPhMA.

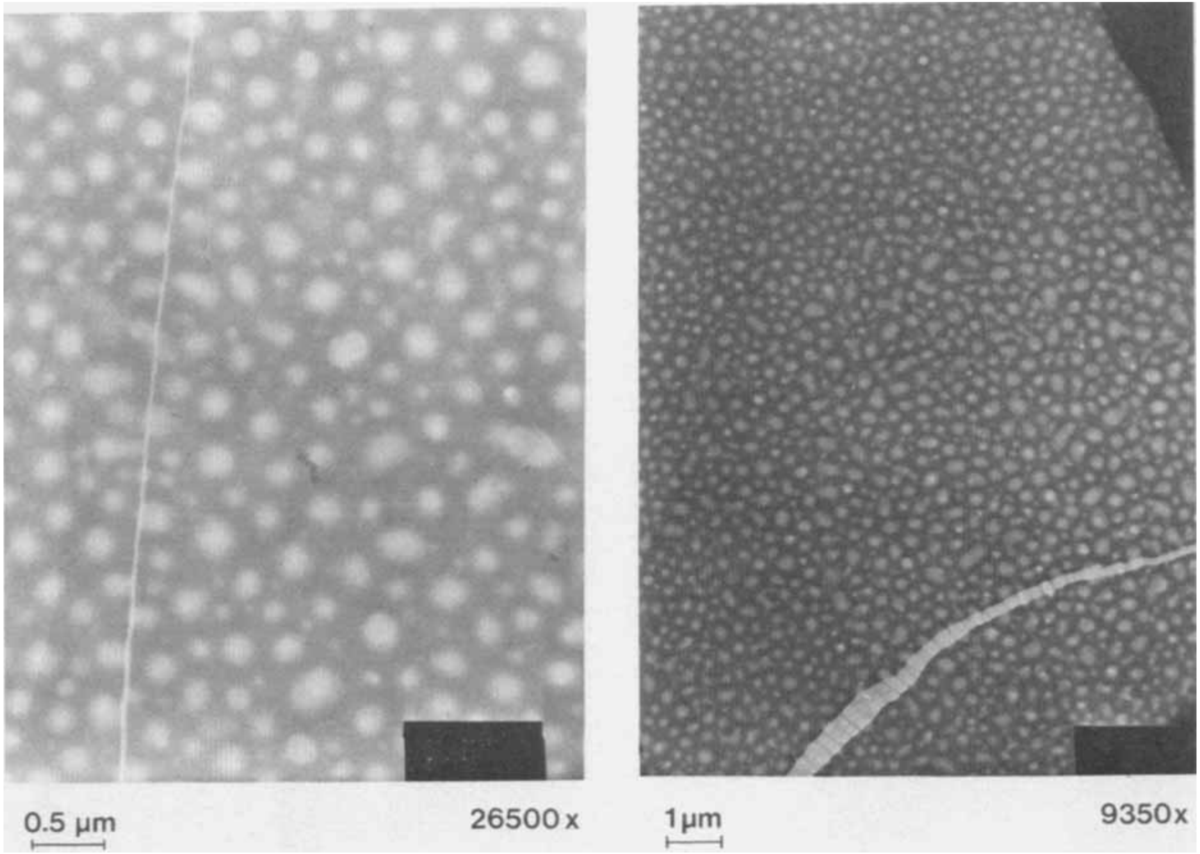


FIG. 8. Electron micrographs of PS-PnBuMA block copolymer recorded from thin film coated directly on the grid from 1% THF solution.

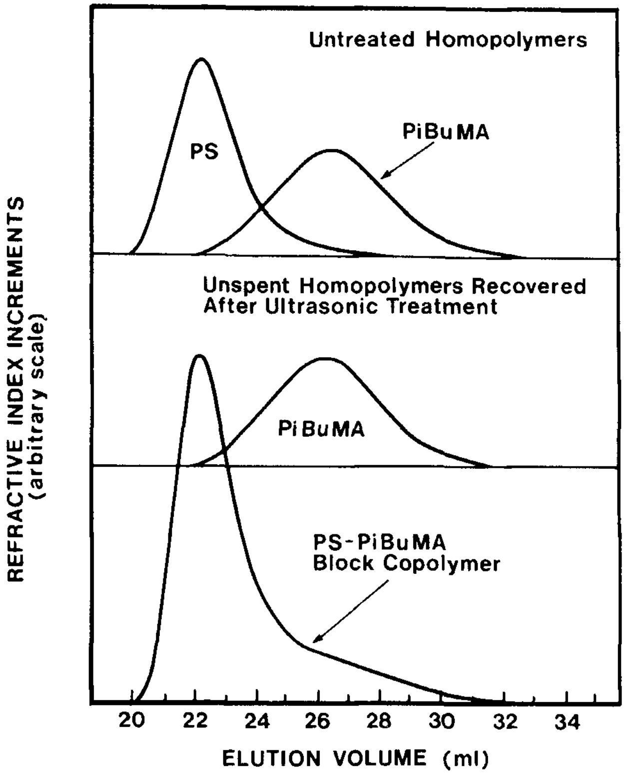


FIG. 9. GPC chromatograms of polymers involved in the block copolymerization of PS and PiBuMA.

traces of PS, leaving behind 2.6 g block copolymer (Fig. 7) PS-PiBuMA (77% PS, 23% PiBuMA) with $\overline{M}_w = 1.1 \times 10^6$, $\overline{M}_n = 4.25 \times 10^5$, $[\eta] = 2.66$ dL/g, and $k_H = 0.38$. These molecular weights were computed from the GPC chromatograms shown in Fig. 9.

In Fig. 10 are presented the electron micrographs of the block copolymer PS-PiBuMA recorded using three different methods of film coating; viz., (a) direct evaporation of 1% THF solution of the polymers on carbon-coated grids, (b) evaporation of 1% THF solution of the polymer on a glass slide, followed by lifting of the thin film by immersing the glass slide in water and mounting the thin film on the electron microscopic grid, (c and d) casting a film of the polymer on water surface and mounting the film on the grid. It is evident that the technique of film preparation of the block copolymer plays an important role in the resultant morphological behavior. Based

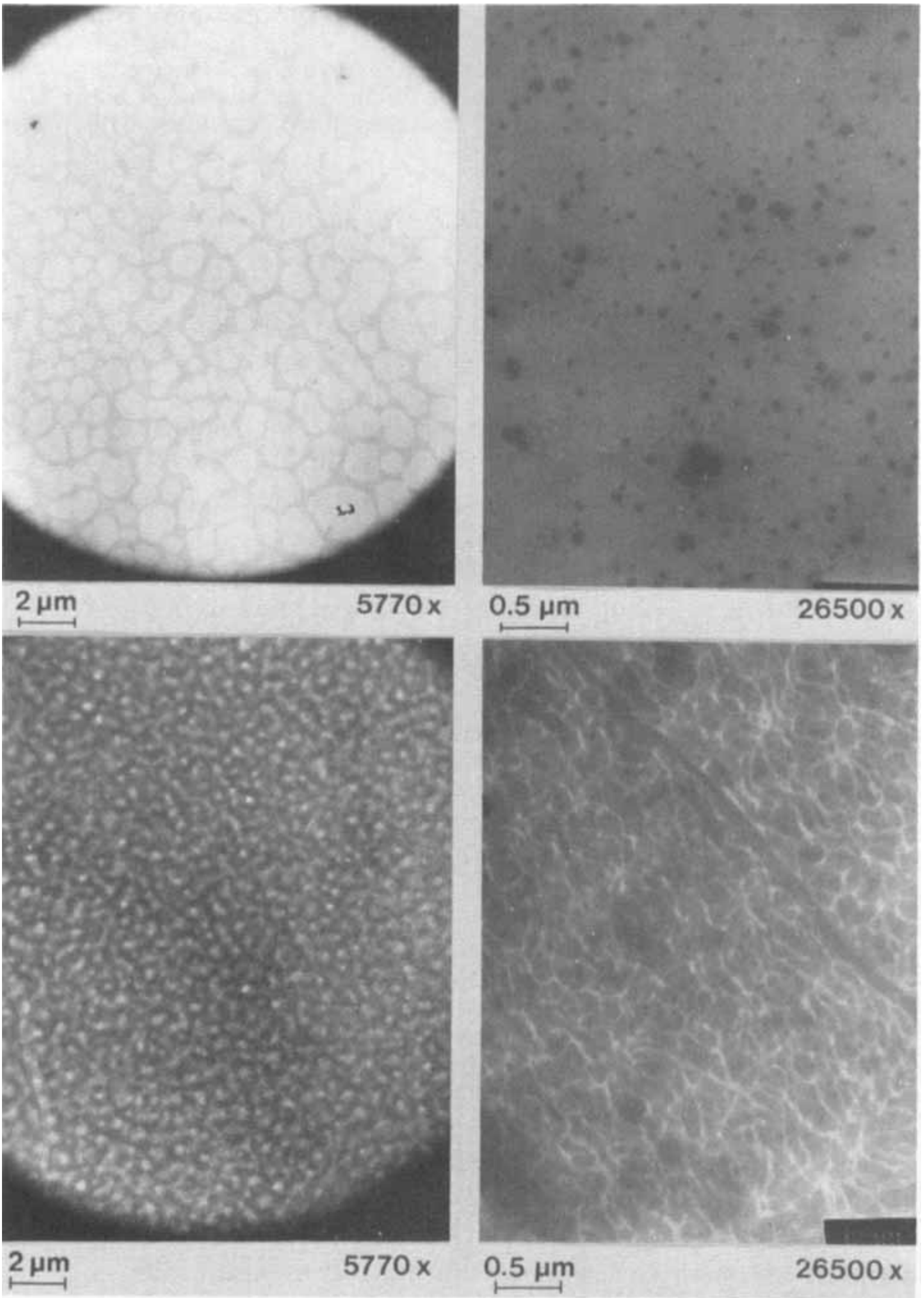


FIG. 10. Electron micrographs of PS-PiBuMA block-copolymer. Upper lift: Thin film from THF solution on the grid. Lower left: Thin film from glass slide deposited on the grid. Right: Thin films of the polymer on the water surface mounted on the grid.

on the electron micrographs, one can only say that this sequence copolymer does not exhibit any domain structure, and instead of being a highly ordered block copolymer, it is a scrambled copolymer with little order of sequences.

Polystyrene (PS)-Poly(phenyl Methacrylate) (PphMA)

2.0 g PS ($\overline{M}_w = 9.0 \times 10^5$, $\overline{M}_w/\overline{M}_n = 1.1$ $[\eta] = 2.25$ dL/g) and 2.0 g PPhMA ($\overline{M}_w = 2.35 \times 10^5$, $\overline{M}_w/\overline{M}_n = 4.5$, $[\eta] = 0.25$ dL/g, $k_H = 0.44$) were dissolved in 175 mL toluene, purged with nitrogen for 30 min, and sonicated at 27°C for 180 min. Evaporation of solvent yielded a mixture of dry polymers from which 100 mg PS ($\overline{M}_w = 2.1 \times 10^5$, $\overline{M}_n = 1.1 \times 10^5$) was recovered with cyclohexane while subsequent washing with mixtures of (heptane + acetone) and (acetone + acetonitrile) yielded 800 mg of PPhMA ($\overline{M}_w = 1.72 \times 10^5$, $\overline{M}_n = 5.0 \times 10^4$, $[\eta] = 0.21$ dL/g, $k_H = 0.0$), leaving behind 3.1 g of block copolymer (Fig. 7) PS-PPhMA (60% PS, 40% PPhMA) with $\overline{M}_w = 3.75 \times 10^5$, $\overline{M}_n = 1.0 \times 10^5$, $[\eta] = 0.74$ dL/g, $k_H = 0.53$). These molecular weights were computed from the GPC chromatograms shown in Fig. 11. Isopropanol is a nonsolvent while acetone, acetone + acetonitrile, and acetone + heptane are solvents for PPhMA.

Polystyrene (PS)-Poly(cyclohexyl Methacrylate) (PCHMA)

2.0 g PS ($\overline{M}_w = 1.8 \times 10^6$, $\overline{M}_w/\overline{M}_n = 1.45$, $[\eta] = 4.8$ dL/g) and 2.0 g PCHMA ($\overline{M}_w = 2.54 \times 10^5$, $\overline{M}_w/\overline{M}_n = 6.6$, $[\eta] = 0.365$ dL/g, $k_H = 0.65$) were dissolved in 175 mL toluene, purged with nitrogen for 30 min, and sonicated at 27°C for 180 min. Evaporation of solvent yielded a mixture of dry polymers from which 700 mg of PCHMA ($\overline{M}_w = 2.5 \times 10^5$, $\overline{M}_w/\overline{M}_n = 7.0$) were recovered with acetone while subsequent washings with cyclohexane yielded only traces of PS, leaving behind 3.3 g of blend (Fig. 12) PS-PCHMA (PS 60%, PCHMA 40%) with $\overline{M}_w = 4.0 \times 10^5$, $\overline{M}_n = 1.0 \times 10^5$, $[\eta] = 0.80$ dL/g, and $k_H = 0.62$. These molecular weights were computed using the GPC chromatograms shown in Fig. 13. Butanol was found to be a solvent for PCHMA as well as for PS.

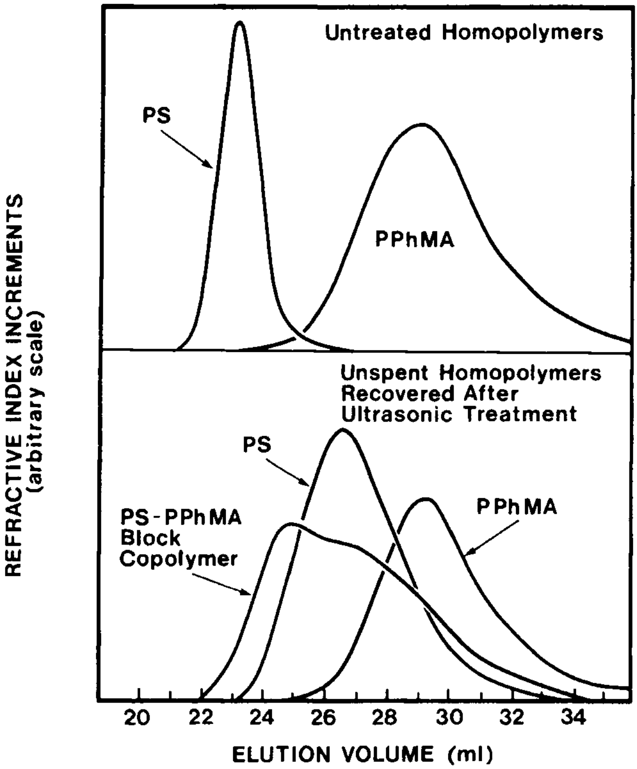


FIG. 11. GPC chromatograms of polymers involved in the block copolymerization of PS and PPhMA.

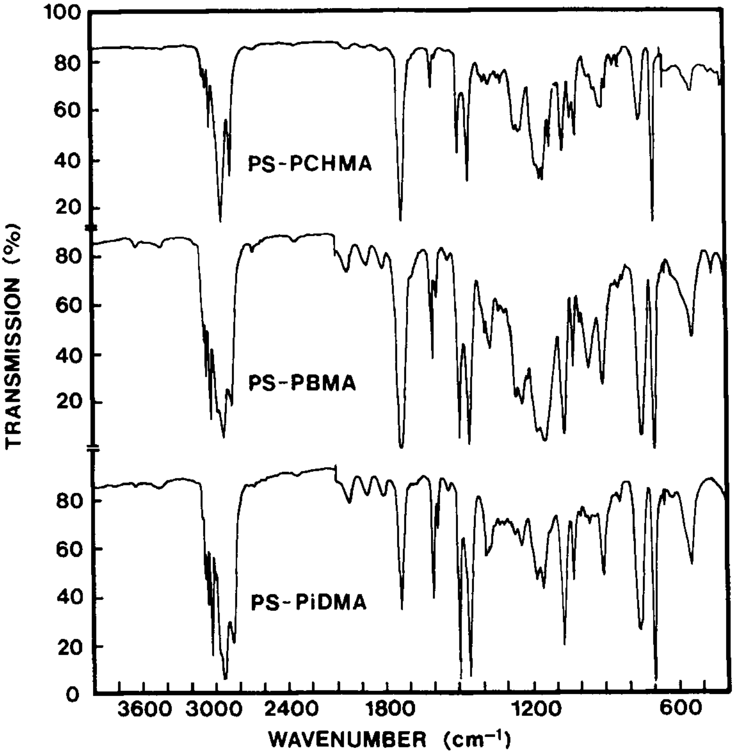


FIG. 12. IR spectra of the insoluble products recovered in the block copolymerization of PS with PCHMA, PBMA, and PiDMA.

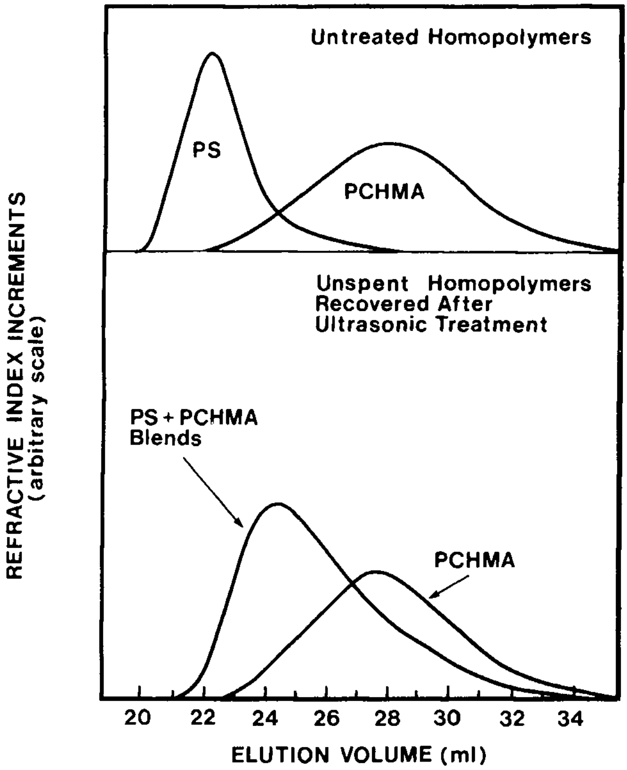


FIG. 13. GPC chromatograms of polymers involved in the block copolymerization of PS and PCHMA.

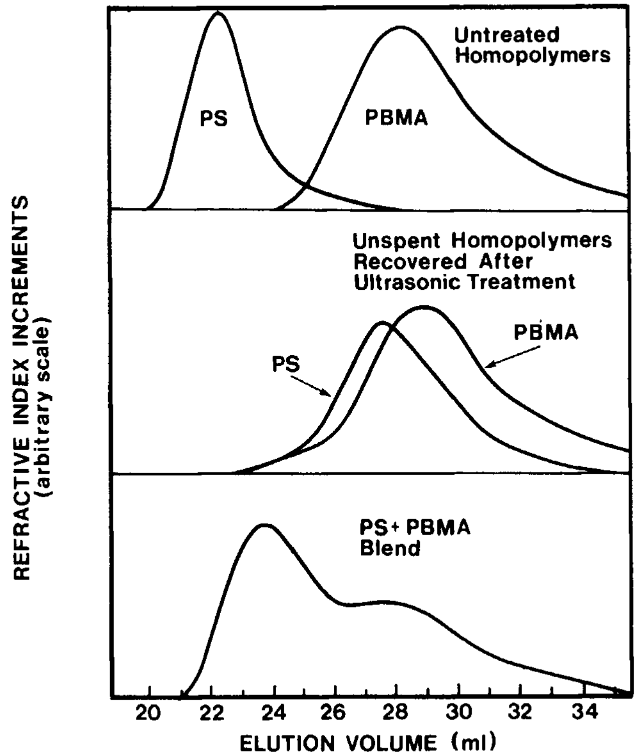


FIG. 14. GPC chromatograms of polymers involved in the block copolymerization of PS and PBMA.

Polystyrene (PS)-Poly(benzyl Methacrylate) (PBMA)

2.0 g PS($\bar{M}_w = 1.8 \times 10^6$, $\bar{M}_w/\bar{M}_n = 1.45$, $[\eta] = 4.8$ dL/g) and 2.0 g PBMA ($\bar{M}_w = 1.9 \times 10^5$, $\bar{M}_w/\bar{M}_n = 6.35$, $[\eta] = 0.22$ dL/g, $k_H = 0.0$) were dissolved in 175 mL toluene, purged with nitrogen for 30 min, and sonicated for 180 min at 27°C. Evaporation of solvent yielded a mixture of dry polymers from which 100 mg PS ($\bar{M}_w = 1.3 \times 10^6$, $\bar{M}_n = 7.06 \times 10^3$) was recovered with cyclohexane while subsequent washings with a mixture of methyl ethyl ketone (200 mL) and isopropanol (800 mL) followed by acetone yielded 500 mg PBMA ($\bar{M}_w = 3.05 \times 10^5$, $\bar{M}_n = 3.0 \times 10^4$, $[\eta] = 0.26$ dL/g, and $k_H = 0.42$) contaminated with PS, leaving behind 3.4 g block copolymer (Fig. 12) PS-PBMA (56% PS, 44% PBMA) with $\bar{M}_w = 3.59 \times 10^5$, $\bar{M}_n = 5.2 \times 10^4$, $[\eta] = 0.94$, dL/g,

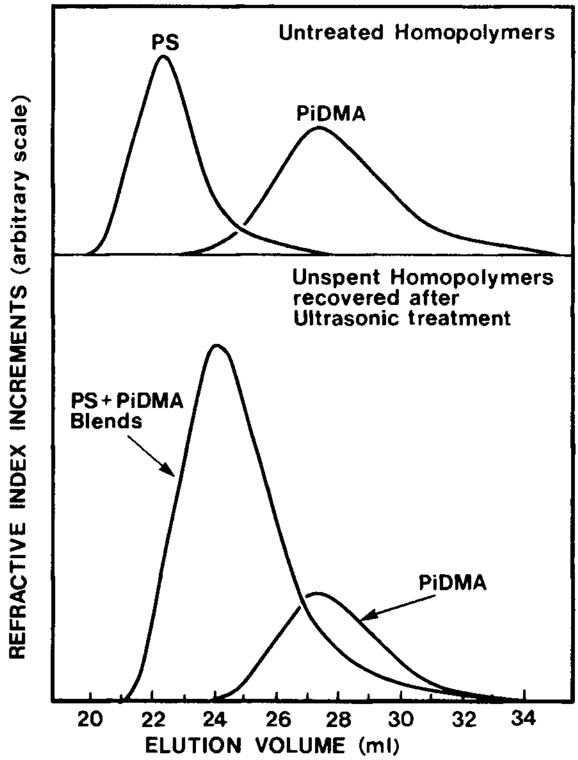


FIG. 15. GPC chromatograms of polymers involved in the block copolymerization of PS and PiDMA.

and $k_H = 0.45$. These molecular weights were computed using the GPC chromatograms shown in Fig. 14.

Polystyrene (PS)-Poly(isodecyl Methacrylate) (PiDMA)

2.0 g PS ($\overline{M}_w = 1.8 \times 10^6$, $\overline{M}_w/\overline{M}_n = 1.45$, $[\eta] = 4.8$ dL/g) and 2.0 g PiDMA ($\overline{M}_w = 2.6 \times 10^5$, $\overline{M}_w/\overline{M}_n = 3.66$) were dissolved in 175 mL toluene, purged with nitrogen, and sonicated at 27°C for 180 min. Evaporation of solvent yielded a mixture of dry polymers from which 1.7 g of PiDMA ($\overline{M}_w = 2.63 \times 10^5$, $\overline{M}_n = 1.13 \times 10^5$) was recovered with a mixture of isopropanol (800 mL) + methyl ethyl ketone (200 mL) while subsequent washing with cyclohexane yielded only traces of PS, leaving behind 2.3 g of blend (Fig. 12) PS-PiDMA (PS 86%, PiDMA 14%) with $\overline{M}_w = 5.0 \times 10^5$, $\overline{M}_n = 2.2 \times 10^5$, $[\eta] = 1.25$ dL/g, and $k_H = 0.46$. These molecular weights were computed using the GPC chromatograms shown in Fig. 15.

Polystyrene (PS)-Poly(hexyl Methacrylate) (PHMA))

1.75 g PS ($\overline{M}_w = 1.8 \times 10^6$, $\overline{M}_w/\overline{M}_n = 1.45$, $[\eta] = 4.8$ dL/g) and 2.5 g PHMA ($\overline{M}_w = 1.12 \times 10^5$, $\overline{M}_w/\overline{M}_n = 2.8$, $[\eta] = 0.49$ dL/g, $k_H = 0.45$) were dissolved in 175 mL toluene, purged with nitrogen for 30 min, and sonicated at 27°C for 210 min. Evaporation of solvent yielded a mixture of dried polymers from which 150 mg PS ($\overline{M}_w = 2.32 \times 10^5$, $\overline{M}_n = 9.07 \times 10^4$) was recovered with cyclohexane while subsequent washings with isopropanol followed by a mixture of heptane + acetone and finally with n-pentanol yielded 2.5 g PHMA ($\overline{M}_w = 1.0 \times 10^5$, $\overline{M}_n = 3.0 \times 10^4$, $[\eta] = 0.38$ dLg, $k_H = 0.33$), leaving behind (not a block copolymer) 1.5 g pure PS which did not dissolve in cyclohexane but was soluble in THF and had $\overline{M}_w = 4.5 \times 10^5$, $\overline{M}_n = 2.95 \times 10^5$, $[\eta] =$ 1.5 dL/g, and $k_H = 0.25$. These molecular weights were computed using the GPC chromatograms in Fig. 16.

Polystyrene (PS)-Poly(hexadecyl Methacrylate) (PHDMA)

1.75 g PS ($\overline{M}_w = 1.8 \times 10^6$, $\overline{M}_w/\overline{M}_n = 1.45$, $[\eta] = 4.8$ dL/g) and 2.25 g PHDMA ($\overline{M}_w = 1.53 \times 10^6$, $\overline{M}_w/\overline{M}_n = 5.8$, $[\eta] = 0.51$ dL/g, $k_H = 0.48$) were dissolved in 175 mL toluene, purged with nitrogen for 30 min, and sonicated at 27°C for 210 min. Evaporation of solvent yielded a mixture of dried polymers from which 250 mg PS ($\overline{M}_w = 2.2 \times 10^5$, $\overline{M}_n = 1.0 \times 10^5$) was recovered with cyclohexane while subsequent washings with a mixture of heptane (600 mL) and acetone (300 mL) followed by n-pentanol yielded 2.25 g PHDMA ($\overline{M}_w = 1.17 \times 10^6$, $\overline{M}_n = 3.0 \times 10^5$, $[\eta] = 0.42$ dL/g, $k_H = 0.45$), leaving behind 1.5 g homopolymer PS ($\overline{M}_w = 3.53 \times 10^5$, $\overline{M}_n = 2.4 \times 10^5$, $[\eta] = 1.33$ dL/g, $k_H = 0.13$) which could not be dissolved in cyclohexane but was soluble in THF. These molecular weights were computed using the GPC chromatograms shown in Fig. 17 and are presented in Table 2.

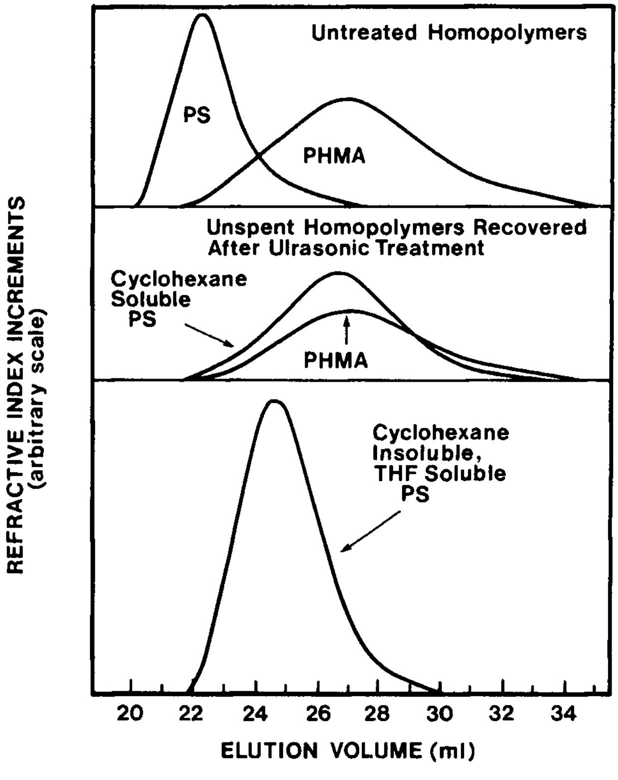


FIG. 16. GPC chromatograms of polymers involved in the block copolymerization of PS and PHMA.

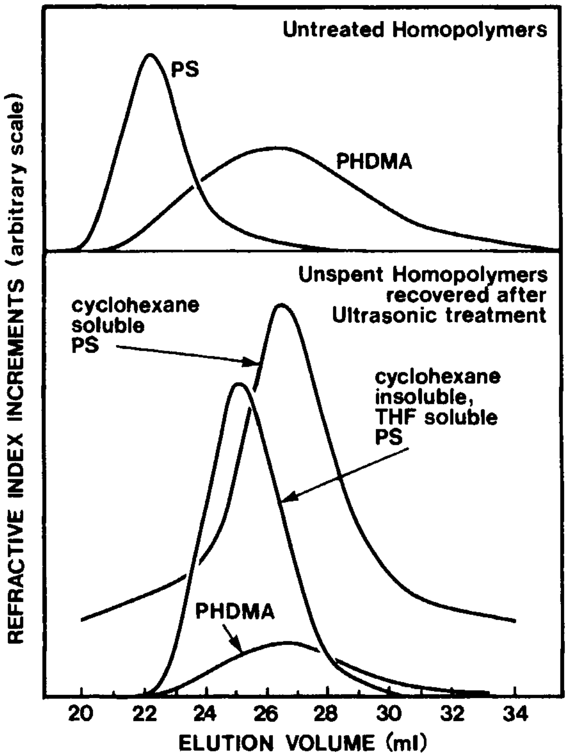


FIG. 17. GPC chromatograms of polymers involved in the block copolymerization of PS and PHDMA.

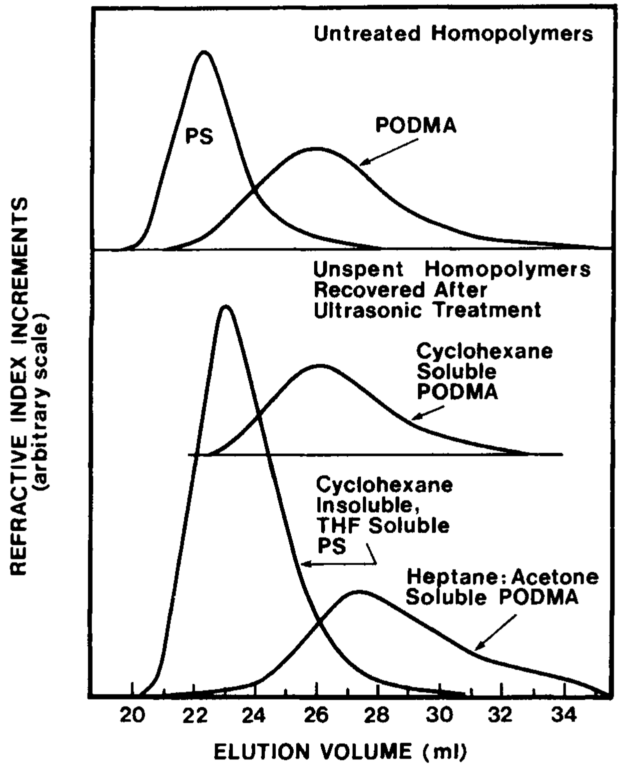


FIG. 18. GPC chromatograms of polymers involved in the block copolymerization of PS and PODMA.

Polystyrene (PS)-Poly(octadecyl Methacrylate) (PODMA)

1.0 g PS ($\overline{M}_w = 1.8 \times 10^6$, $\overline{M}_w/\overline{M}_n = 1.45$, $[\eta] = 4.8$ dL/g) and 1.0 g PODMA ($\overline{M}_w = 6.8 \times 10^5$, $\overline{M}_w/\overline{M}_n = 6.0$, $[\eta] = 0.49$ dL/g, $k_H = 0.43$) were dissolved in 175 mL toluene, purged with nitrogen for 30 min, and sonicated at 27°C for 210 min. Evaporation of solvent yielded a mixture of polymers from which 450 mg of PODMA ($\overline{M}_w = 7.0 \times 10^5$, $\overline{M}_n = 10 \times 10^5$) was recovered with cyclohexane while subsequent washings with a mixture of heptane (600 mL) and acetone (300 mL) yielded 550 mg PODMA ($\overline{M}_w = 6.0 \times 10^5$, $\overline{M}_n = 1.07 \times 10^5$), leaving behind 1.0 g PS homopolymer with $\overline{M}_w = 7.15 \times 10^5$, $\overline{M}_n = 4.7 \times 10^5$,

$[\eta] = 2.55$ dL/g, and $k_H = 0.40$. These molecular weights were computed using the GPC chromatograms shown in Fig. 18. Acetone, acetonitrile, n-butanol, methanol, dimethylsulfoxide, methyl ethyl ketone, and n-heptane are nonsolvents while cyclohexane, cyclohexanone, n-butylacetate, and mixtures of heptane (50%) and acetone (50% are solvents for PODMA. Solvent pairs [e.g., heptane (50%) + acetonitrile (50%), or cyclohexane (60%) + methanol (40%)] which do not mix well and yield two layers can also be used for separating a mixture of PS and PODMA as the latter polymer is soluble in the upper layer while PS remains insoluble.

Polystyrene (PS)-Poly(lauryl Methacrylate) (PLMA)

2.0 g PS ($\overline{M}_w = 9.0 \times 10^5$, $\overline{M}_w/\overline{M}_n = 1.3$, $[\eta] = 2.25$ dL/g) and 2.0 g of PLMA (or dodecyl methacrylate) ($\overline{M}_w = 2.9 \times 10^5$, $\overline{M}_w/\overline{M}_n = 3.1$, $[\eta] = 0.38$ dL/g, $k_H = 0.38$) were dissolved in toluene, purged with nitrogen, and sonicated for 180 min at 27°C. Evaporation of solvent yielded dried polymers from which 200 mg of PS ($\overline{M}_w = 3.17 \times 10^5$, $\overline{M}_n = 1.8 \times 10^5$) was recovered with cyclohexane while subsequent washings with a mixture of heptane (600 mL) and acetone (300 mL) followed by n-pentanol yielded 2.0 g of PLMA ($\overline{M}_w = 2.1 \times 10^5$, $\overline{M}_n = 6.0 \times 10^4$), leaving behind 1.7 g PS homopolymer with $\overline{M}_w = 3.35 \times 10^5$, $\overline{M}_n = 2.17 \times 10^5$, $[\eta] = 1.15$ dL/g, and $k_H = 0.35$. These molecular weights were computed using the GPC chromatograms shown in Fig. 19. Isopropanol and acetonitrile are nonsolvents for PLMA.

Polystyrene (PS)-Poly(isobornyl Methacrylate) (PIBoMA)

2.0 g PS ($\overline{M}_w = 9.0 \times 10^5$, $\overline{M}_w/\overline{M}_n = 1.3$, $[\eta] = 2.25$ dL/g) and 4.5 g PiBoMA ($\overline{M}_w = 4.0 \times 10^5$, $\overline{M}_w/\overline{M}_n = 3.0$, $[\eta] = 0.72$ dL/g, $k_H = 0.49$) were dissolved in toluene, purged with nitrogen for 30 min, and sonicated at 27°C for 240 min. Evaporation of solvent yielded dried products from which 4.0 g of mixture of (450 mg PS + 3.5 g PiBoMA) with $\overline{M}_w = 3.0 \times 10^5$, $\overline{M}_n = 1.0 \times 10^5$, $[\eta] = 0.56$ dL/g, and $k_H = 0.41$ was recovered with cyclohexane while 1.0 g of PiBoMA ($\overline{M}_w = 1.4 \times 10^5$ $\overline{M}_n = 9.0 \times 10^3$) was obtained with cyclohexanol, leaving behind 1.5 g PS homopolymer ($\overline{M}_w = 3.8 \times 10^5$, $\overline{M}_n = 2.8 \times 10^5$, $[\eta] = 1.24$ dL/g,

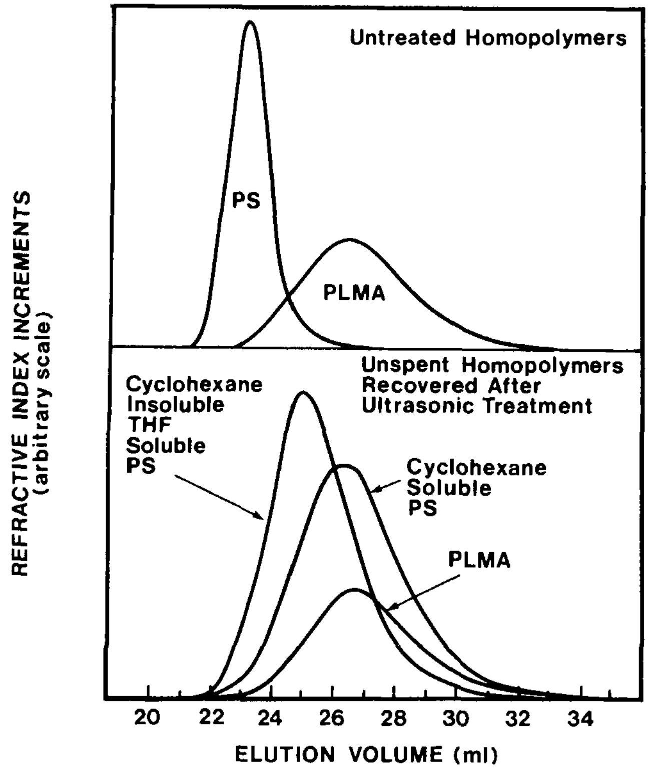


FIG. 19. GPC chromatograms of polymers involved in the block copolymerization of PS and PLMA.

$k_H = 0.35$). These molecular weights were computed using the GPC chromatograms shown in Fig. 20. Acetonitrile, acetone, cyclohexane, and cyclohexanol are solvents for PiBoMA.

CONCLUSIONS

1. In the ultrasonic solution degradation of PS in the presence of PRMA, when the substituent R was methyl, ethyl, isopropyl, n-butyl, or phenyl, scrambled sequence copolymers with segments from PS and PRMA were obtained. The overall $\overline{M}_w$ of these copolymers ranged between 4.0×10^5 and 6.0×10^5 with the exception of PS-PiBuMA which showed a $\overline{M}_w$ value of 11.0×10^5. The overall polydispersity ($\overline{M}_w/\overline{M}_n$ ratio) ranged between 1.7 to 3.75. Huggins

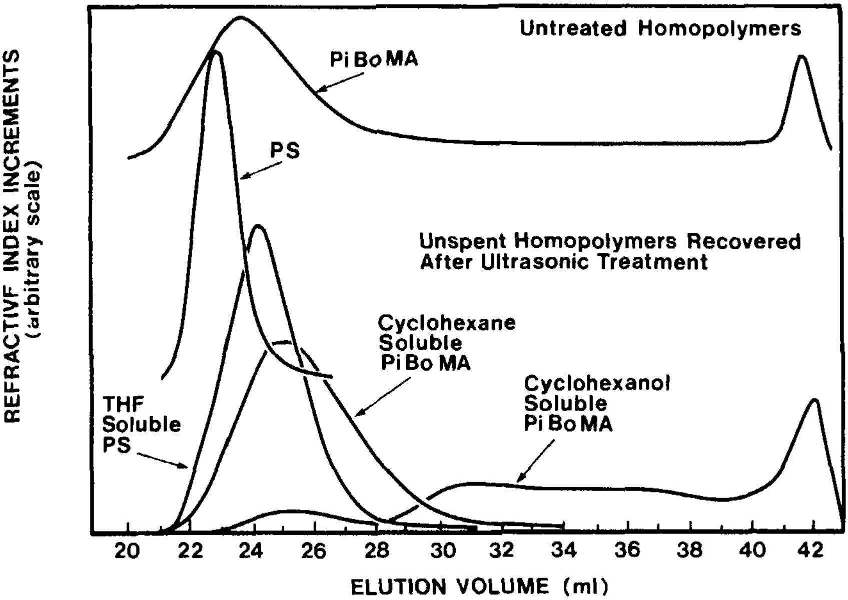


FIG. 20. GPC chromatograms of polymers involved in the block copolymerization of PS and PiBoMA.

coefficient of all these copolymers varied from 0.17 to 0.5, suggesting a random coil configuration.

2. In the other ultrasonic solution degradations of PS and PRMA mixtures, when the substituents were cyclohexyl, benzyl, or isodecyl, the IR spectra of the end product did show the presence of PS and PRMA peaks. This, however, may be due to an imperfection in the technique of separation of homo and block copolymers and not because of the formation of sequence copolymers. This conclusion is based on the large polydispersity index of the end products (free of homopolymers). Huggins coefficients of these end products also suggest a random coil configuration.

3. In the ultrasonic solution degradation of PS and PRMA, when the substituent R was hexyl, isodecyl, hexadecyl, actadecyl, lauryl, and isobornyl, there were no sequence polymers formed. The decrease in the intrinsic viscosity of the recovered homopolymers and shifts of their GPC chromatograms toward the low molecular weight end suggest that on sonification of a PRMA having a bulkier substituent R, in the presence of PS, the two homopolymers do degrade yielding radicals which, however, do not recombine.

4. Degradation of PS in the presence of poly(alkyl methacrylates) is found to be dependent on the chain stiffness of the latter polymers.

Further studies are being carried out on ultrasonic solution degradations of PS as well as poly(alkyl methacrylate) homopolymers alone at 27 and -20°C to follow their rate of chain breaking. It is hoped that by improving the rate of chain breaking of poly(alkyl methacrylates) at lower temperatures, sequence copolymers carrying a major fraction of the softer component (PRMA) and a minor fraction of the hard component (PS) can be prepared. This was not possible at 27°C (see Table 1).

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