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# Styryl-Telechelic Polyisobutylenes. II. Amphiphilic Sequential Copolymers of Styryl-Telechelic Polyisobutylenes with Vinyl Acetate or N-Vinyl-2-pyrrolidone

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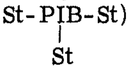
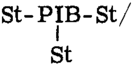
## ABSTRACT

Styryl-telechelic polyisobutylenes (i.e., linear and three-arm star polyisobutylenes capped with polymerizable p-styryl endgroups St-PIB-St and  $\mathrm{St{-}P}\underset{\substack{|\\ \mathrm{St}}}{\mathrm{I}}\mathrm{B{-}St}$) have been copolymerized with vinyl acetate VAc or N-vinyl-2-pyrrolidone VP by conventional free radical techniques. The products obtained with St-PIB-St/VAc systems were soluble, most likely branched block copolymers of isobutylene IB and VAc, whereas those prepared with St-PIB-St/VP or  $\mathrm{St{-}P}\underset{\substack{|\\ \mathrm{St}}}{\mathrm{I}}\mathrm{B{-}St}$/VP combinations were networks consisting of PIB and poly(N-vinyl-2-pyrrolidone) PVP sequences. That the copolymerization of St-PIB-St with VAc results in soluble products and that with VP yields networks is due to the very different reactivities of styrene with VAc

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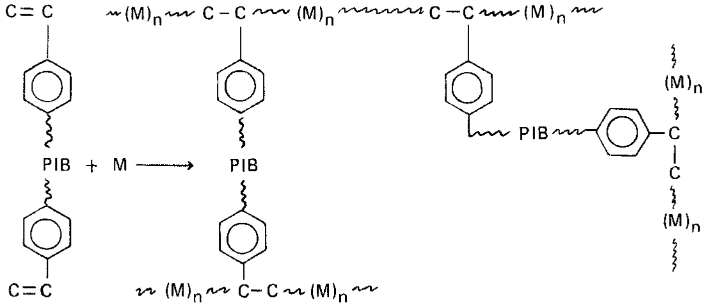
and with VP. Hydrolysis of VAc units in PIB-PVAc block copolymers gave vinyl alcohol VA units, i.e., these products are branched block copolymers consisting of random VAc/VA copolymer sequences connected to PIB sequences. The overall composition of these soluble amphiphilic materials was determined from conversion and molecular weight data and by $^1$H-NMR spectroscopy; their mechanical properties were examined by stress-strain measurements. The composition of amphiphilic PVP-PIB networks was calculated from conversion and elemental analysis data. These gels were found to bind both water-soluble dyes (methyl orange) and hydrocarbons (benzene). The first binding constant $k_1$ that characterizes the binding of methyl orange by these PVP-PIB networks is one order of magnitude larger than that characteristic of the binding of this dye by cross-linked PVP or by serum albumin.

## INTRODUCTION

Amphiphilic polymers (i.e., polymers that dissolve or swell in both water and hydrocarbon solvents) are of great current interest for a variety of potential applications in medicine, agriculture, etc. [1-7]. It occurred to us that the copolymerization of linear or three-arm star styrene-telechelic polyisobutylene macromers St-PIB-St and St-PIB-St with a pendant St (whose synthesis is the subject of a preceding publication [8]) with monomers M that produce water-soluble polymers would be a route to novel amphiphilic materials (the formalism shows copolymerization of St-PIB-St with M only):

$$\begin{array}{c} \text{St-PIB-St} \\ | \\ \text{St} \end{array}$$

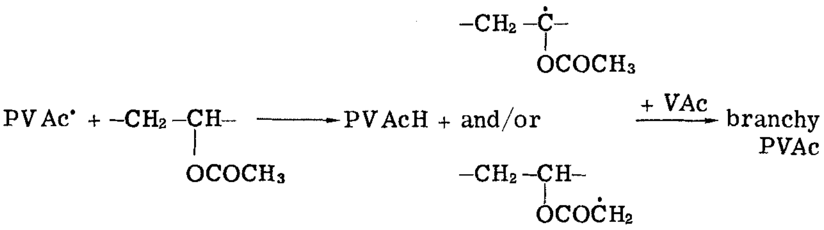


where $(M)_n$ = water-soluble sequences and n indicates averages of repeat units whose exact value is determined by the nature of M and reaction conditions.

The styrene endgroup should be readily copolymerizable under conventional free radical conditions with a large variety of monomers that yield desirable water-soluble macromolecules, e.g., N-vinyl-2-pyrrolidone, hydroxyethyl methacrylate, acrylic acid, acrylamide. Among the possible candidates we selected VP for further detailed investigation because of the relatively low cost of this monomer and because PVP is biocompatible and is used in medicinal applications. The copolymerization of St-PIB-St with VP was expected to yield water and hydrocarbon swellable networks suitable for delayed drug release, water purification, and similar applications.

The detailed characterization of these amphiphilic networks was anticipated to be very difficult. Since these networks consist of two incompatible (see later) sequences, i.e., PIB and PVP, meaningful cross-link density (swelling) measurements could not be carried out because of the unavailability of suitable equations like those developed for the characterization of homogeneous (one component) networks, e.g., the Flory-Rehner equation [10]. Also, because these materials are insoluble, only few spectroscopic techniques (e.g., IR) could be considered. Thus the thought occurred to us to prepare more readily characterizable soluble branched block copolymers by coreacting under free radical conditions St-PIB-St with VAc. The reactivity ratios of VAc and St are quite different, so these monomers do not give true random copolymers [9]; indeed, St may be regarded as an inhibitor in VAc polymerization (i.e., the propagating vinyl acetate radical PVAc$^{\bullet}$ rapidly reacts with St and the styrene radical so formed PVAcSt$^{\bullet}$ is unable to initiate the polymerization of VAc). We postulated that mixtures of VAc and St-PIB-St, i.e., systems containing VAc and a low molar concentration of styryl functions, would behave as VAc polymerizations inhibited by St and thus yield soluble products most likely consisting of one St-PIB-St unit connected to one, two, three, or four PVAc sequences. Scheme 1 helps to visualize the processes involved.

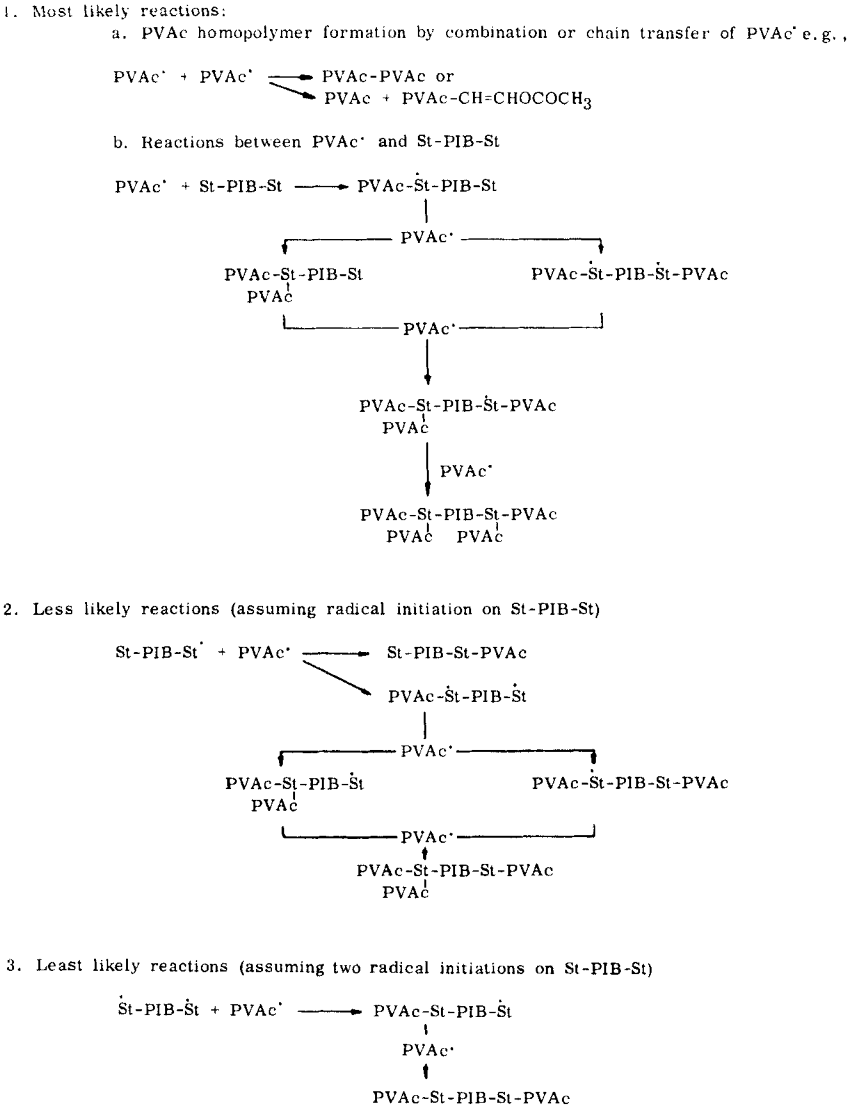
In addition to the reactions considered in Scheme 1, branchy-branch formation in the PVAc sequences by chain transfer to PVAc may also occur:



$$\mathrm{PVAc^{\bullet}} + -\mathrm{CH_2}-\underset{\mathrm{OCOCH_3}}{\underset{|}{\mathrm{CH}}}- \longrightarrow \mathrm{PVAcH} + \begin{array}{c} -\mathrm{CH_2}-\underset{\mathrm{OCOCH_3}}{\underset{|}{\overset{\bullet}{\mathrm{C}}}}- \\ \text{and/or} \\ -\mathrm{CH_2}-\underset{\mathrm{OCO\dot{C}H_2}}{\underset{|}{\mathrm{CH}}}- \end{array} \xrightarrow{+\,\mathrm{VAc}} \begin{array}{c}\text{branchy} \\ \text{PVAc}\end{array}$$

According to this analysis, the most likely products are branched block copolymers consisting of one St-PIB-St unit and several PVAc sequences.

In view of the complex structure of these block copolymers, it is difficult to develop a precise nomenclature. We have adopted Ceresa's proposition [11] and use the prefix [br] to express branching and [c.l.]



SCHEME 1. Branched block copolymer formation by free radical copolymerization of VAc and St-PIB-St.

for cross-linking. Thus the abbreviation for the soluble branched amphiphilic product obtained from VAc and St-PIB-St will be [br]-poly(vinyl acetate-b-isobutylene) or brPVAc-b-PIB; it should be kept in mind that the branch points are styryl units (see Scheme 1) and the PVAc sequences may be branchy. Similarly, the insoluble products obtained by copolymerizing VP with St-PIB-St or $\text{St-P}\underset{\underset{\text{St}}{|}}{\text{I}}\text{B-St}$ will be abbreviated by [c.l.]poly(N-vinyl-2-pyrrolidone-b-isobutylene) or c.l.PVP-b-PIB, and it should be kept in mind that the cross-linking sites are styryl units.

This paper concerns the preparation of novel amphiphilic products brPVAc-b-PIB from VAc plus St-PIB-St, and c.l.PVP-b-PIB from VP plus St-PIB-St, and VP plus $\text{St-P}\underset{\underset{\text{St}}{|}}{\text{I}}\text{B-St}$, by conventional free radical copolymerization techniques, the characterization of the products, and some physical studies.

## EXPERIMENTAL

### Materials

The synthesis of linear and three-arm star styryl-telechelic PIB's (St-PIB-St and $\text{St-P}\underset{\underset{\text{St}}{|}}{\text{I}}\text{B-St}$) has been described [8].

Vinyl acetate (VAc) (Aldrich) and N-vinyl-2-pyrrolidone (VP) were purified by distillation at 73 and 98°C/9 mmHg, respectively. Azobisisobutyronitrile, AIBN (Eastman), was recrystallized from methanol. Benzene (Fisher Scientific Co.) was washed with sulfuric acid, then washed several times with water, stored over $CaCl_2$, and freshly distilled. Other solvents were used as received. Methyl orange MeO (Aldrich) was used as received.

### Techniques

$^1H$-NMR analyses were carried out using a Varian Associates T-60 NMR spectrometer. Solutions of approximately 10% polymer in $CCl_4$ were employed.

IR spectra were obtained by the use of a Perkin-Elmer 521 Grating Infrared Spectrophotometer. UV spectra were recorded on a Perkin-Elmer 559A UV/VIS Spectrophotometer. Aqueous methyl orange ($\lambda_{max}$ = 464) and benzene ($\lambda_{max}$ = 256 nm) solutions were used to construct calibration curves.

GC measurements were carried out by using a Hewlett-Packard 7610A gas chromatograph equipped with SE30 columns at 70°C. Benzene in toluene was used to construct the calibration curve.

Elemental analyses were done by Galbraith Laboratories. $T_g$ data were obtained by a DuPont 990 Thermal Analyzer at three scanning rates and the data were extrapolated to 0°C/min.

Stress-strain data were obtained on an Instron Universal Testing Instrument with 1 in/min crosshead speed at room temperature.

## Free Radical Polymerizations

Copolymerizations of St-PIB-St with VAc, St-PIB-St with VP, and St-$\underset{\underset{\text{St}}{|}}{\text{PIB}}$-St with VP were carried out in ampules using AIBN initiator and benzene solvent in degassed systems at 60°C for 72 h and at 50°C for 34 h. Homopolymers and unreacted styryl telechelic PIB's were removed by fractional precipitation. Thus, brPVAc-b-PIB's in benzene were precipitated three times into n-hexane to remove St-PIB-St, then redissolved in benzene and precipitated three times into methanol to remove PVAc. The insoluble c.l.PVP-b-PIB's were recovered by precipitation into methanol and were extracted sequentially with n-hexane and water at room temperature for 24 h to remove residual styryl-telechelic PIB and PVP, respectively.

## Binding Experiments with c.l.PVP-b-PVP

### Binding of Methyl Orange

The first binding constant $k_1 = nk$ (where k is the intrinsic binding constant and n is the number of binding sites per $10^5$ g VP units) [6, 8] of c.l.PVP-b-PIV was determined as follows: Six mixtures containing 0.10 g polymer and 5 mL of aqueous methyl orange MeO ([MeO] = 0.75 × $10^{-3}$ to 3.75 × $10^{-5}$ M) were prepared and stored at 25°C for 48 h. The polymers swell and imbibe MeO, and equilibrium is reached in less than 48 h, as determined by preliminary experiments. After 48 h the MeO concentration in the supernatant liquid was determined by UV spectroscopy. The quantity of dye absorbed by the network was obtained by subtracting the amount of MeO in the water phase from that initially added to the system. Binding isotherms were obtained by plotting r, mole MeO bound per $10^5$ g network, against log **C**, equilibrium dye concentration in the aqueous phase in mol/L.

The $k_1$ values were determined from the slopes of linear 1/r' against 1/C plots (Klotz plots) where r' is the mole MeO bound per $10^5$ g VP units in the network [12].

Cross-linked PIB was prepared by cross-linking of St-$\underset{\underset{\text{St}}{|}}{\text{PIB}}$-St ($\overline{M}_n$ = 15,200) in bulk with AIBN (0.2 wt%) at 60°C for 3 d, then extracting with n-hexane (room temperature, 24 h), adding fresh AIBN (0.2 wt%) and continuing the heating for two additional days. Conversion to network was ~85%. The binding of MeO by the PIB networks was investigated by the same technique described above.

The rate of MeO desorption was qualitatively studied by adding a solution of 0.01 g MeO in 20 mL water to 1 g of a network. After equilibrium (48 h) the network loaded with MeO was removed from the solution and placed into 20 mL of fresh water. After a suitable time interval the quantity of MeO desorbed into the water was determined by UV spectroscopy. The water was removed, replaced by fresh water, and the procedure was repeated until the bound MeO was completely recovered.

### Binding of Benzene

One gram amphiphilic network was added to a solution of $8 \times 10^{-3}$ mL benzene in 20 mL water ($4.47 \times 10^{-3}$ $\underline{M}$, 50% of saturation [13], and after 48 h (equilibrium) the benzene content of the supernatant was determined by GC and UV.

### Hydrolysis of brPVAc-b-PIB

To a solution of 1 g brPVAc-b-PIB in 10 mL benzene was added 0.3 g NaOH in 2 mL MeOH and stirred for 4 h at ambient temperature. After washing several times with water, the polymer was recovered from the benzene solution by evaporating the solvent.

## RESULTS AND DISCUSSION

### Copolymerization of Linear Styryl-Telechelic PIB with VAc

A series of St-PIB-St/VAc copolymerizations have been carried out. Results are shown in Table 1, and Figs. 1 and 2 show representative $^1$H-NMR and IR spectra of the products. According to these spectra both the PIB and PVAc moieties are present, and since the products have been obtained after fractional precipitation (see Experimental), the presence of block copolymers is proven.

As shown by the data in Table 1, by increasing the St-PIB-St concentration (i.e., St inhibitor) in the feed, the PVAc content in the copolymer decreases.

According to Scheme 1, the copolymer is most likely highly branched, consisting of a central PIB sequence to which are attached through styryl groups one, two, three, or four PVAc sequences. In regard to structure, it is difficult to go beyond this statement on the basis of the information on hand.

The fraction recovered by precipitation into n-hexane (see Experimental) was PIB possessing the initial $\overline{M}_n$ of the St-PIB-St which indi-

TABLE 1. Copolymerization of St-PIB-St ($M_1$) with VAc ($M_2$)[a]

| Monomer concentration [M] | | Converted to copolymer | | IB Content of the copolymer, mol-% by | | $\overline{M}_n$[c] of copolymer |
|---|---|---|---|---|---|---|
| $M_1 \times 10^3$[b] | $M_2 \times 10$ | St-PIB-St (%) | VAc (%) | $^1$H-NMR | From conversion | |
| 2.56 | 2.16 | 88.8 | 36.5 | 25.7 | 28.0 | 42,400 |
| 5.20 | 2.16 | 78.8 | 34.1 | 45.3 | 42.4 | 22,200 |
| 7.20 | 2.16 | 81.2 | 33.4 | 50.7 | 53.2 | 19,400 |
| 7.89 | 2.16 | 61.9 | 29.7 | 48.4 | 49.8 | 20,600 |
| 10.80 | 2.16 | 80.2 | 29.8 | 61.1 | 64.4 | 15,400 |

[a] In 20 mL benzene with 0.5% AIBN initiator at 60°C for 72 h.

[b] The $\overline{M}_n$ of St-PIB-St was 7800.

[c] Estimated by knowing the overall composition of the copolymer and the $\overline{M}_n$ of the styryl-telechelic PIB.

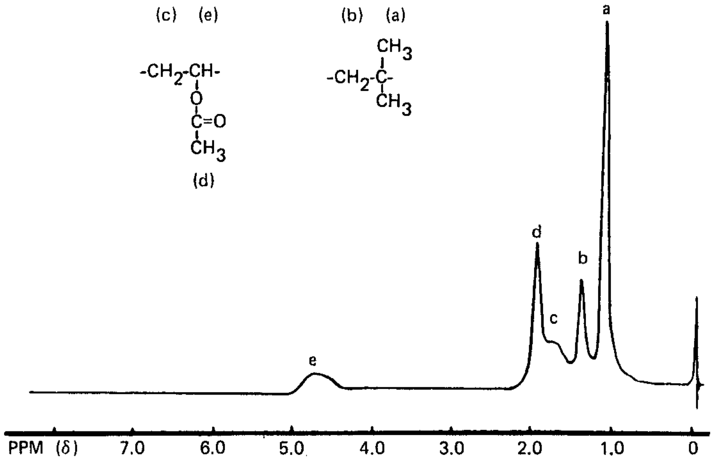


FIG. 1. $^1$H-NMR spectrum of St ∼∼∼PIB∼∼∼St/VAc copolymer. 50.7 mol% IB in polymer.

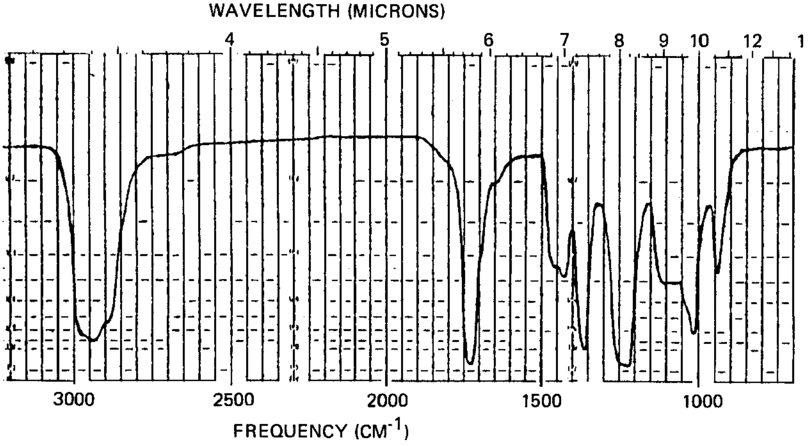


FIG. 2. IR spectrum of St∼∼∼PIB∼∼∼St/VAc copolymer. 50.7 mol% IB in polymer.

cates that recombination of St-PIB-St• radicals did not occur. This may be due to the low St• concentrations or to the decreased mobility of St-PIB-St•, particularly at higher conversions where the viscosity of the system has increased. Precipitation into methanol yielded PVAc which suggests combination of PVAc radicals or chain transfer processes (see Introduction).

Glass transition temperatures of brPVAc-b-PIB samples have been determined. According to DSC measurements, a high and a low temperature $T_g$ was found, indicating extensive phase segregation into PVAc ($T_g$ = 26 to 29°C) and PIB ($T_g$ = -60 to -63°C) domains. The $T_g$'s of authentic PVAc and PIB are 32°C [14] and -73°C [14], respectively.

Select physical-mechanical properties of brPVAc-b-PIB and partially hydrolyzed brPVAc-b-PIB samples have been investigated. The latter materials can formally be regarded as random VAc/VA copolymer sequences held together by PIB sequences. PVA contains extensive H bridges yielding strong aggregates and consequently improved mechanical properties. Figure 3 shows stress-strain curves of select samples containing similar amounts of IB units. The partially hydro-

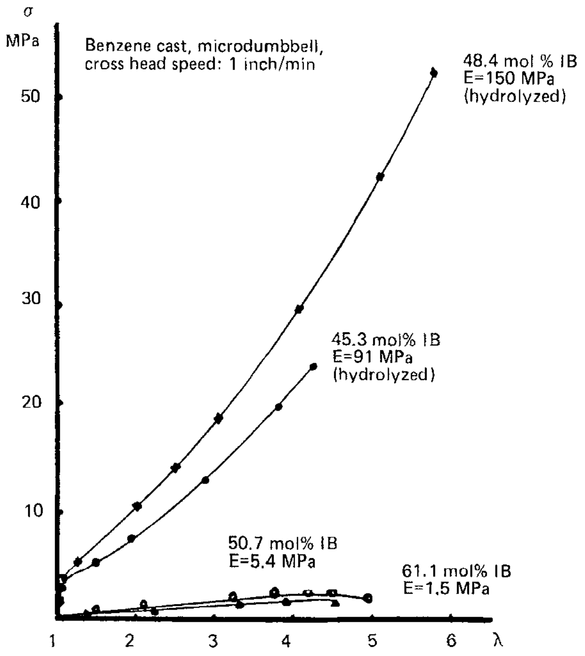


FIG. 3. Stress-strain data of ST∼∼∼PIB∼∼∼St/VAc copolymer before and after hydrolysis.

lyzed samples exhibit a dramatic increase in mechanical properties. These excellent properties are the more remarkable considering the soluble nature of these materials.

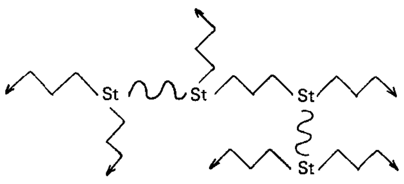
## Copolymerization of Linear and Three-Arm Star Styryl-Telechelic PIB's with VP

The copolymerization of St-PIB-St and $\text{St-}\underset{\text{St}}{\underset{|}{\text{PIB}}}\text{-St}$ with VP has been studied and the results are compiled in Table 2.

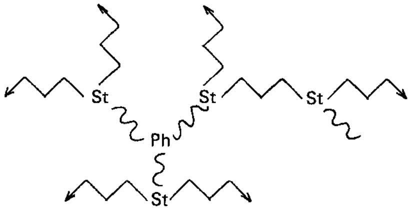
Since the free radical copolymerization of St with VP produces random products ($r_{St} = 15.7$; $r_{VP} = 0.045$) [15], we expected random networks in styryl-telechelic PIB's/VP systems as well. In line with these r values, increasing styryl-telechelic PIB concentrations in the feed yielded increased PIB concentrations in the network.

In view of the much higher reactivity of St than VP, network formation probably occurs at the early stages of copolymerization. At higher conversions, particularly in the presence of chain transfer, VP homopolymer will arise and can be removed by extraction. By increasing the styryl endgroup concentration, the amount of extractable PVP decreases.

The networks formed in these copolymerizations contain two polymer sequences, i.e., PIB and PVP, most likely connected in a random manner. Thus, these networks could be described by two $\overline{M}_c$'s. One of the $\overline{M}_c$'s, the $\overline{M}_n$ of PIB between two styryl groups $\overline{M}_{c,PIB}$, is identical to the $\overline{M}_n$ of the styryl-telechelic PIB in case of the linear St-PIB-St. In contrast, $\overline{M}_{c,PIB}$ for the three-arm star PIB is equal to 1/3 of the $\overline{M}_n$ of the $\text{St-}\underset{\text{St}}{\underset{|}{\text{PIB}}}\text{-St}$ starting material. The $\overline{M}_{c,PIB}$ in this case is the $\overline{M}_n$ of the PIB sequence between a styryl cross-linking site and the central phenyl group in the three-arm star PIB. The following scheme helps to visualize these matters:



Network produced from
St-PIB-St/VP combinations



Network produced from
$\text{St-}\underset{\text{St}}{\underset{|}{\text{PIB}}}\text{-St}$/VP combinations

TABLE 2. Copolymerization of Styryl-Telechelic PIB ($M_1$) with VP ($M_2$)[a]

| Monomer concentration, [M] | | | Converted to copolymer | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $M_1 \times 10^3$ | $M_2$ | $M_2/M_1$ in the feed | AIBN (%) | PIB (%) | VP (%) | Total VP conversion (%) | IB content in the copolymer, mol% from conversion | $M_2/M_1$ in the copolymer | $\overline{M}_{c,PVP}$ | $T_g$'s of copolymer[b] (°C) |
| Linear St-PIB-St; $M_n$ or $M_{c,PIB} = 7{,}800$ | | | | | | | | | | |
| 1.4 | 0.8 | 551 | 0.2 | 92 | 44 | 100 | 34.1 | 270 | 29,500 | -70/166 |
| 5.8 | 0.8 | 138 | 0.2 | 84 | 78 | 99 | 52.3 | 128 | 14,200 | -68/173 |
| 11.5 | 0.8 | 69 | 0.2 | 81 | 84 | 99 | 66.2 | 71 | 7,900 | -62/176 |
| Three-Arm Star $\text{St-}\underset{\substack{\vert \\ \text{St}}}{\text{PIB}}\text{-St}$; $\overline{M}_n = 15{,}200$; $\overline{M}_{c,PIB} = 5{,}070$ | | | | | | | | | | |
| 5.7 | 1.13 | 200 | 0.2 | 85 | 62 | 95 | 64.8 | 146 | 8,300 | - |
| 5.7 | 1.13 | 200 | 2.0 | 89 | 30 | 71 | 79.5[c] | 69 | 3,900 | -58/176 |
| 5.7 | 0.56 | 100 | 2.0 | 83 | 44 | 98 | 83.3 | 53 | 3,100 | -60/168 |

[a] In 20 mL benzene at 50°C for 34 h.

[b] $T_{gPIB} = -73°C$ [14], $T_{gPVP} = 154°C$, determined in this work.

[c] 78.9% by elemental analysis.

where ╱╲╱╲ = $\overline{M}_c$,PVP

∿∿∿ = $\overline{M}_{c,PIB}$

The other $\overline{M}_c$, i.e., the $\overline{M}_n$ of PVP between two styryl cross-linking sites $\overline{M}_{c,PVP}$, may be estimated by knowledge of the overall composition of the network and the $\overline{M}_n$ of the styryl-telechelic PIB, and assuming essentially complete network formation. For example, for the network containing 66.2% PIB (cf. Table 2) $\overline{M}_{c,PIB}$ = 7800 and $\overline{M}_{c,PVP}$ = 7900.

Table 2 also shows $T_g$ data. The presence of two $T_g$'s indicates extensive phase segregation in these materials. The fact that the high temperature $T_g$ ($T_{g,PVP}$) increases with increasing PIB content may be due to increased network density. The low temperature $T_g$ ($T_{g,PIB}$) is lower for the network obtained with the St-PIB-St (-70 to -62° C) than that with the $\text{St-}\underset{\substack{| \\ \text{St}}}{\text{PIB}}\text{-St}$ (-60 to -58°C). This phenomenon is due to the higher $\overline{M}_c$ in the former network.

The binding of small organic molecules such as MeO and benzene by c.l.PVP-b-PIB networks has been studied. The amount of MeO bound by the amphiphilic network r as a function of MeO equilibrium concentration in the aqueous phase C has been determined. Figure 4 shows the binding isotherms. The first binding constant $k_1$, i.e., the parameter

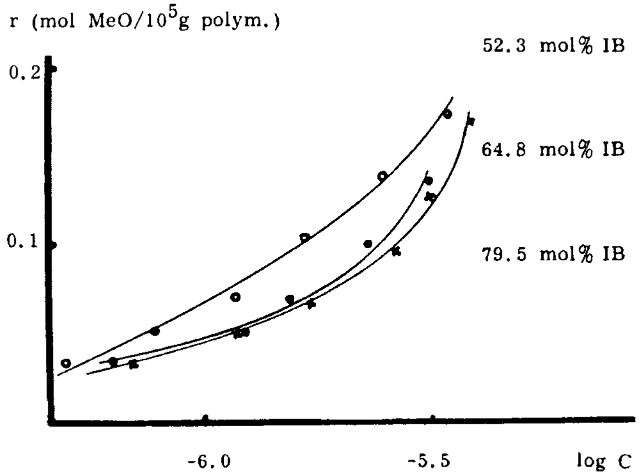


FIG. 4. Extent of binding of MeO by St∿∿PIB∿∿St/VP copolymer.

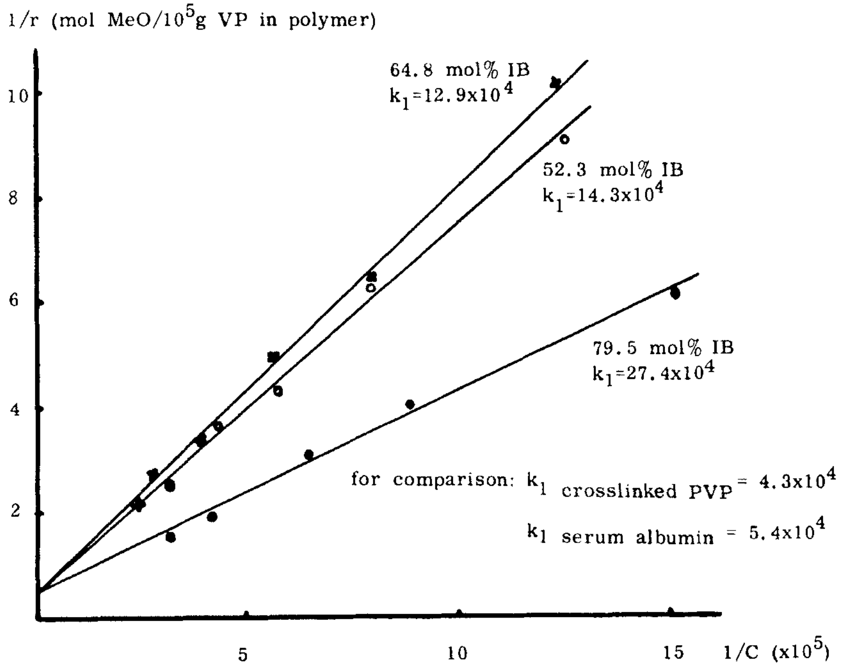


FIG. 5. Relationship between 1/r and 1/C (Klotz plot).

that quantitatively characterizes the binding ability of the networks, has subsequently been obtained from the slope of linear Klotz plots shown in Fig. 5. Interestingly, the $k_1$'s of our amphiphilic networks are significantly higher than those of the hydrophilic gels, i.e., cross-linked PVP or serum albumin, materials known to possess exceptionally high binding ability for MeO [16, 17].

The binding of MeO by these networks does not decrease with increasing IB content. In fact, the network containing the largest amount of PIB exhibits the highest $k_1$ in spite of the fact that the cross-linked PIB was found not to bind MeO.

The strong interaction between the MeO and these amphiphilic networks has been confirmed by studying the rate of MeO desorption from one of these gels. According to the results of a representative desorption experiment shown in Fig. 6, the desorption of MeO from c.l.PVP-b-PIB networks is a rather slow process. Such amphiphilic networks may hold promise from delayed drug release applications.

These novel networks show excellent binding ability not only for MeO but also for apolar molecules such as benzene. An experiment has been carried out in which water contaminated by benzene ([benzene] = $4.47 \times 10^{-3}$ $\underline{M}$) was contacted with an amphiphilic network containing

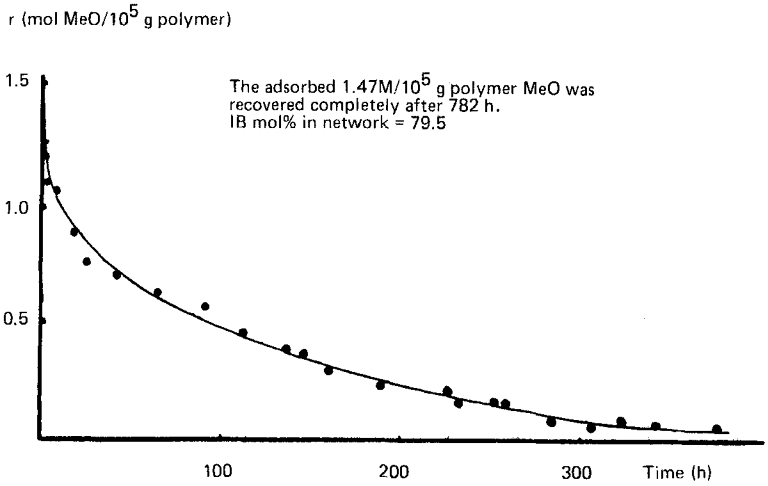


FIG. 6. Desorption of MeO bound on St~~~PIB~~~St/VP copolymer.

83.3 mol% PIB and after 48 h the benzene concentration decreased significantly ([benzene] = $0.25 \times 10^{-3}$ M). Evidently strong hydrophobic interaction exists between apolar PIB blocks and benzene, and between the apolar moiety of PVP and benzene.

## ACKNOWLEDGMENT

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