# Polystyrene Modifications.  I.  Styrene Copolymers*

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This study was undertaken to discover polystyrene modifications having thermal properties comparable to and craze resistance higher than polystyrene.  Crazing is the stress-induced development of small cracks which reflect light in the polymer surface;[1-3] these stresses may result from thermal expansion or contraction, the application of mechanical force, or the presence of solvent[4] or monomer.  Maxwell and Rohm[3] have demonstrated that crazing is not reversible at room temperature but is reversible above the glass transition temperature.  Sauer and Hsiao[5] have shown that, through a limited stress range, the rate of propagation of crazing is a linear function of time and stress.

Reduced crazing is reported to result when strains in the system are released.  Pinsky[6] has indicated that crazing in polystyrene and polymethyl methacrylate can be prevented by an annealing procedure.  Maxwell and Rohm[7] have demonstrated that strain-free polystyrene does not fracture under applied load until a strain of 2% is reached, whereas in the presence of solvent-like materials such as $n$-heptane or kerosene, crazing and ultimate fracture occur at strains as low as 0.2%.

Many of the measures recommended for combatting undesirable effects of crazing do not actually produce an improved polymer.  For example, strain-free sheets of polystyrene can be prepared by careful fabrication techniques, but subsequent application of stresses will still cause crazing. Surface coatings which reduce crazing also alter the physical properties of the surface, often in undesirable ways.

## DISCUSSION

In order to simplify the otherwise involved nomenclature of the copolymers and terpolymers studied, a simple code has been adopted, where S is styrene, B is butadiene, A is acenaphthylene, and M is mineral oil.  Thus, S20A designates a copolymer of styrene and acenaphthylene with monomer ratios preceding polymerization of 80 wt.-% of styrene and 20 wt.-% of acenaphthylene.  Terpolymers are similarly identified.  S20A15B refers to a terpolymer prepared from a mixture of 65 wt.-% styrene, 20 wt.-% acenaphthylene, and 15 wt.-% butadiene.

In the expectation that copolymer modifications more highly craze resistant than polystyrene itself would possess glass transition temperatures $(T_g)$ below the $T_g$ of polystyrene, an initial copolymer having $T_g$ appreciably above 100°C. was desired. The poly(styrene-co-acenaphthylene) system was selected for study, since polyacenaphthylene has a $T_g$ of 214°C., and relatively small amounts of added acenaphthylene resulted in large increases in the $T_g$.

The glass transition temperatures of styrene–acenaphthylene copolymers, plotted as a function of monomer mixture composition in Figure 1, fall on a line drawn from the $T_g$ of polystyrene to that of polyacenaphthylene. The $T_g$ was measured by differential thermal analysis, and precise values were difficult to determine because the second-order transition ex-
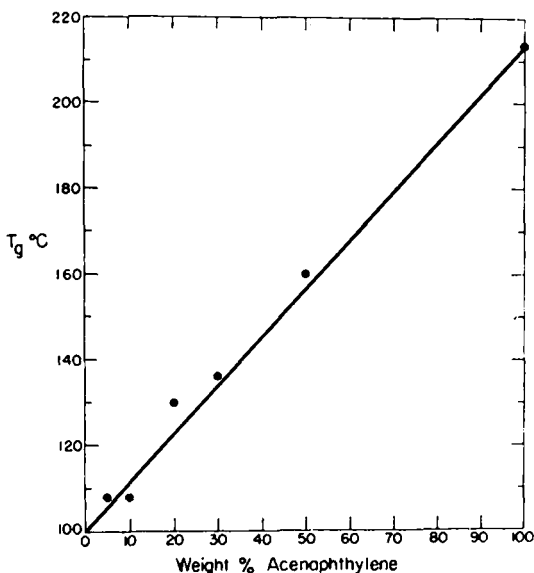


Fig. 1. Second-order transition temperature of styrene-co-acenaphthylene polymers as a function of composition: (●) emulsion polymerization.

tended over a wide temperature range. Sometimes the components of the copolymer seemed to be partially incompatible and transitions would be obtained for polystyrene and polyacenaphthylene as well as for the copolymer composition.

Preparation of poly(styrene-co-acenaphthylene) by mass polymerization at 92°C., with 1% benzoyl peroxide, produced low-molecular-weight copolymers. Amyl sodium did not catalyze the polymerization of styrene–acenaphthylene mixtures and the Ziegler catalyst (aluminum triethyl + titanium tetrachloride) gave very low yields. Thermal polymerization (no catalyst) at 120–125°C. for 10 days gave slightly higher viscosities than those obtained from mass-polymerized samples. Emulsion polymerization at 30°C., using a redox catalyst system, gave excellent yields and high

viscosities up to the limit of emulsifiability of the monomer mixture (50% acenaphthylene). The results of these polymerizations are summarized in Table I.

TABLE I
Copolymerization of Styrene and Acenaphthylene

| Ace-naph-thylene, wt.-% | Mass polymerization[a] | | Thermal polymerization[b] | | Emulsion polymerization[c] | |
|---|---|---|---|---|---|---|
| | $\{\eta\}$ | $T_g$, °C. | $\{\eta\}$ | $T_g$, °C. | $\{\eta\}$ | $T_s$ °C. |
| 0 | 0.90 | 100 | 0.80 | 100 | 4.1 | 100 |
| 5 | | | 0.63 | 104.5 | 3.08 | 108 |
| 10 | 0.42 | 107 | 0.54 | 106.5 | 1.71 | 108 |
| 20 | 0.35 | 107 | 0.44 | 108 | 1.25 | ~130 |
| 30 | 0.33 | ~130 | 0.36 | 109.5 | 0.79 | 136 |
| 40 | 0.30 | | | | 0.81 | |
| 50 | 0.30 | | 0.30 | —[d] | 0.62 | ~160 |
| 60 | 0.23 | | | | | |
| 70 | 0.26 | | | | | |
| 75 | | | 0.33 | ~178 | | |
| 80 | 0.24 | | | | | |
| 90 | 0.20 | | | | | |
| 100 | 0.15 | | 0.32 | 205 (214) | | |

[a] One per cent benzoyl peroxide; 5 days at 92°C.

[b] No catalyst; 10 days at 120–125°C.

[c] With a redox catalyst; 44 hr. at 30°C. for 0, 5, 10% acenaphthylene samples; 44 hr. at 30°C. plus 96 hr. at 40°C. for 20, 30, 50% acenaphthylene samples.

[d] Incompatible.

The $T_g$ of emulsion-polymerized S20A copolymers varied from 127–130°C. Extrusion of a sample into a monofilament at 275°C. resulted in degradation of the polymer from an initial intrinsic viscosity of 1.25 to a viscosity of 0.85. Other samples were highly purified before extrusion and gave monofilaments which were generally smooth, clear, brittle, and slightly yellow. Brittleness decreased after the monofil had been oriented. Properties of the monofils after 150% stretching at 140°C. are listed in Table II.

The greatest degradation during extrusion occurred with highly purified samples which were in a fluffy condition, indicating that breakdown during extrusion was a problem not of residual catalyst or of impurities in the polymer sample but rather of entrapped air in the polymer mass.

Attempts were made to improve craze resistance of S20A by introducing into the polymerization mixture comonomers which would add flexibility to the chain backbone. The introduction of butadiene even in small amounts caused a severe drop in the $T_g$ (see Fig. 2).

D'Ianni and Sell[3] found that, while the softening point of polystyrene is

TABLE II
Physical Properties of S20A Extruded at 275°C, Stretched 150% at 135–145°C.

| Polymer | Inherent viscosities | | Young's Modulus $\times 10^{-4}$, kg./cm.$^2$ | Yield, kg./cm.$^2$ | Tensile, kg./cm.$^2$ | Elongation at $T_\theta$ | |
|---|---|---|---|---|---|---|---|
| | Before extrusion | After extrusion | | | | break, % | °C. |
| Monofil, Koppers atactic polystyrene[a] | — | — | 3.4 | 630 | 810 | <4 | 100 |
| Plax PB polystyrene (sheet) | — | — | 3.5 | — | 810 | 3.6–4 | 100 |
| S20A | 1.25 | 0.85 | 3.9 | 570 | 570 | 3.2 | 127 |
| S20A[b] | 1.65 | 0.94 | 5.3 | 850 | 1100 | 4.5 | 130 |
| S20A[c] | 1.52 | 0.74 | 5.0 | 1100 | 1100 | 5.0 | 130 |

[a] Stretched 210% at 110°C.
[b] Polymer frozen out of emulsion, washed thoroughly with water and methanol, dried in vacuum oven.
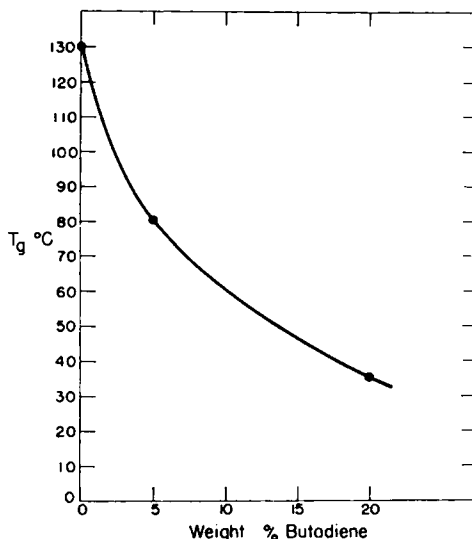[c] Reprecipitated polymer.

Fig. 2. Effect of adding butadiene to S20A polymer.

normally drastically reduced by adding small amounts of butadiene, this effect can be lessened by partial polymerization of styrene prior to addition of butadiene, thus forming a block copolymer (see Fig. 3).

The applicability of this method to styrene:acenaphthylene:butadiene terpolymers was studied. Table III lists the $T_g$ of block terpolymers of S20A formed by adding butadiene after prepolymerization of the styrene and acenaphthylene.

The assignment of definite $T_g$ was difficult because of the broad isotherms obtained. For example, in polymers prepolymerized for 0 and 1.5 hr., the isotherms extended over a 10–15°C. range, while in the other polymers, they extended over twice this temperature range. Also, the presence of a
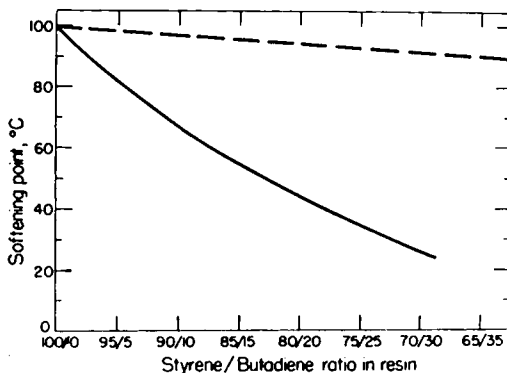


Fig. 3. Polymerization of butadiene with styrene: (—) softening-point curve for normal styrene–butadiene copolymers; (---) softening-point curve for copolymers obtained by partial polymerization of styrene prior to polymerization with butadiene.

TABLE III
Effect of Delayed Addition of Butadiene upon $T_g$

| Polymer compn. | Prepolymer- ization before addn. of buta- diene, hr. | $\{\eta\}$ | $T_g$, °C. |
|---|---|---|---|
| S20A20B | 0 | 1.72 | 35.0 |
| S20A20B | 1.5 | 1.52 | 53.5 |
| S20A20B | 3.0 | 1.24 | 53.0 |
| S20A20B | 4.5 | 0.79 | 76.5[a] |
| S20A20B | 6.0 | 0.91 | 87.5[b] |
| S20A20B | 16.0 | — | —[c] |

[a] In addition, a small baseline shift occurred at (5) 52°C.
[b] In addition, a small baseline shift occurred at ~55°C.
[c] No definite glass transition was observed in the temperature range 24–130°C. An exotherm beginning at 130°C. obscured transitions in the range 130–190°C.

small shift at 52–55°C. with the 4.5- and 6-hr. prepolymerized polymers indicated possible nonhomogeneity of the sample. This was confirmed by extrusion of the 6-hr. sample which gave rough, opaque monofils, indicating incompatibility. Reduction of the amount of butadiene did not yield compatible systems. When the butadiene was added, 6 hr. after initiation of polymerization, S20A15B and S20A10B were incompatible, although the S20A15B polymer was tough and flexible.

The S20A polymer was modified with isoprene in a manner similar to the modification with butadiene. These systems were also incompatible and gave results similar to those of the butadiene-modified polymers. No measurable increases in the $T_g$ of partially prepolymerized samples over those of regular terpolymers could be found.

Attempts to impart flexibility to S20A were made by adding small amounts of mineral oil to the monomer mixture prior to polymerization. The resulting incompatible polymers containing 1 and 3% mineral oil were reprecipitated to remove residual oil, but the polymers, though flexible, were still incompatible. Differential thermal analysis of reprecipitated polymers gave broad isotherms. The $T_g$ of S20A1M was 115–143°C., and the $T_g$ of S20A3M was 140–162°C. A film cast from a solution of S20A polymer to which 3% mineral oil had been added had a $T_g$ of 124°C. This film was not clear, again indicating incompatibility.

Although films cast from butadiene-, isoprene-, or mineral oil-modified S20A polymers were more flexible than those cast from polystyrene, they evidenced no improvement in craze resistance. These results are somewhat surprising in view of the findings of several investigators[9,10] that high-impact polystyrenes do not craze. High-impact types are reported to be mixtures of polystyrene and natural or synthetic rubber, the rubber being present in amounts of 2–10%. Craze resistance is at-

tributed to increased elongation. Above the yield point, however, these polymers become white in the area under stress, indicating a region of strain-induced failure similar to that observed in crazing.

The crazing of butadiene-, isoprene-, or mineral oil-modified S20A polymer may be understood by considering a theory proposed by Hopkins et al.[11] Voids and imperfections in polystyrene would allow gases and vapors of nonsolvents to diffuse readily into the polymer, concentrate at the imperfections, and exert two-dimensional gas pressure to form a crack. Nielsen[4] has demonstrated that exposure of polystyrene to vapors does induce crazing. Since the modified S20A terpolymers were incompatible, it is apparent that imperfections would be present to a greater degree than in polystyrene, and imposed strains would result in the appearance of cracks in these regions.

## EXPERIMENTAL

### Monomers

Liquid monomers were distilled shortly before use to remove inhibitors and were stored in a freezer at $-20°C$. Acenaphthylene, obtained from the Aldrich Chemical Co., was recrystallized from methanol to give glistening yellow plates, m.p. 89–90°C. (uncorrected).

### Polymerizations

*Mass Polymerization of Styrene–*
*Acenaphthylene Copolymers*

Ten grams of monomer mixture and 0.10 g. of benzoyl peroxide were placed in 30 ml., wide-mouth, screw-cap bottles and immersed to just below the neck in a water bath maintained at 90°C. Clear solutions were obtained immediately with all samples except pure acenaphthylene. The temperature of the bath was raised to 92°C., and a clear melt was obtained with the acenaphthylene. After 113 hr. in the water bath, the samples were dried in a vacuum oven at 105°C. for 24 hr. The color varied from clear and colorless for polystyrene to amber for polymers containing increasing amounts of acenaphthylene. Inherent viscosities and the $T_g$ were determined.

*Attempted Polymerization with Amyl*
*Sodium Catalyst*

Ten grams of monomer mixture were dissolved in 75 ml. of dry cyclohexane and 10 ml. of amyl sodium dispersion containing 0.83 meq. of amyl sodium per ml. of hexane was added. The reaction mixture was sealed in a 4-oz. pressure bottle which had been flushed with nitrogen, and then tumbled in a water bath at 5°C. for 65 hr. The mixture was poured into excess methanol to destroy the catalyst and precipitate the polymer. Solid

polymer was obtained from the styrene homopolymerization, but not from styrene–acenaphthylene mixtures.

### Polymerization with Ziegler-Type Catalyst

Ten grams of monomer mixture, 65 g. of cyclohexane, 6 ml. of a 10% solution of triethyl aluminum in cyclohexane, and 1.65 ml. of a 10% solution of titanium tetrachloride in cyclohexane were sealed in a 4-oz. pressure bottle and tumbled in a water bath at 70°C. for 18 hr. After cooling, the sample was poured into 500 ml. of methanol to leach out the catalyst. Homopolystyrene was obtained in good yield and homopolyacenaphthylene in 21% yield, but copolymers were obtained in low yields (~5%).

### Thermal Polymerization

Five grams of monomer mixture were placed in a clear glass vial which had been flushed with nitrogen, and the vial was sealed with an oxygen torch. Polymerization took place (without agitation) in an oven maintained at 120–125°C. After 24 hr., the samples containing 5, 10, 75, and 100% acenaphthylene had formed clear, glassy polymers whose color increased from pale yellow to amber; samples containing 30 and 50% acenaphthylene were opaque, indicating probable incompatibility. The 30% acenaphthylene sample gave two transitions, one at 109.5°C. and the other one at 214°C. (polyacenaphthylene).

### Emulsion Polymerization of Styrene–Acenaphthylene Copolymers

Ten grams of monomer mixture containing up to 50% acenaphthylene (upper limit of solubility of acenaphthylene in styrene at 30°C.) were placed in a 4-oz. pressure bottle. To this were added 24 ml. of distilled water, 0.4 g. of N-oleoyl-N-methyltauramide (OMT), and 0.1 g. of potassium persulfate. The bottle was flushed with nitrogen, capped, and tumbled in a water bath at 30°C. for 44 hr. At the end of this time, samples containing more than 10% acenaphthylene appeared to be incompletely polymerized (indicated by the presence of droplets of monomer in the emulsion). These samples were tumbled for an additional 96 hr. at 40°C. The polymerized samples were poured into half-pint freezer cartons and frozen at −20°C. to break the emulsions. After thawing, the samples were filtered, washed with water until no foam appeared in the filtrate, and then washed with methanol. The granular polymers were dried in a vacuum oven at 30°C. Viscosities and the $T_g$ were determined. Styrene–acenaphthylene copolymers containing 1 to 3% mineral oil were polymerized in the same manner.

### Emulsion Polymerization of Styrene–Acenaphthylene–Butadiene

Twenty grams of monomer mixture, 1 drop of dodecanethiol, and 6 drops of cumene hydroperoxide were added to a solution of 5 mg. of ferric

sulfate, 100 mg. of fructose, 300 mg. of sodium pyrophosphate decahydrate, and 1 g. of OMT in 30 ml. of distilled water in a 4-oz. pressure bottle. Butadiene was added last, and in slight excess, and the tared bottle was allowed to reach correct weight by evaporation of butadiene.    It was immediately capped, and then tumbled in a water bath at 40°C. for 16 hr. The emulsion was treated as described for styrene–acenaphthylene copolymers in the preceding section.

When styrene–acenaphthylene copolymers were prepolymerized before addition of butadiene, the bottle was sealed with a Neoprene-gasketed cap and the butadiene was injected with a hypodermic syringe at the desired time.

Terpolymers of styrene–acenaphthylene with isoprene were made by this same procedure.

## Inherent Viscosity Determinations

Polymer (0.25 g.) was dissolved in 100 ml. of trichlorobenzene.    Determinations were made in an Ubbelohde viscometer at 25°C.

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## Synopsis

The $T_g$ of polystyrene was raised by copolymerization with acenaphthylene.   Although physical properties of S20A polymer equaled or surpassed those of polystyrene, the addition of butadiene, mineral oil, or isoprene to poly(styrene-co-acenaphthylene) drastically reduced the $T_g$.   The reduction of $T_g$ of S20A by the addition of butadiene was less severe when butadiene was added several hours after the polymerization had begun.   The incompatible terpolymers were flexible but showed no improvement in craze resistance. Crazing has been explained as being caused by forces concentrated in regions of irregularities.

## Résumé

La température $T_g$ du polystyrène s'élève par copolymérisation avec l'acénaphtylène. Quoique les propriétés physiques du polymère S20A égale ou surpasse celles du polystyrène, l'addition de butadiène, d'huile minérale ou d'isoprène au poly(styrène-co-acénaphtylène) réduit fortement la température $T_g$.   La réduction de la température du

S20A par addition du butadiène est moins marquée quand on ajoute le butadiène plusieurs heures aprés le début de la polymérisation.    Les polymères ternaires non compatibles sont flexibles mais ne montrent pas d'amélioration dans la résistance au ternissement. On a expliqué la ternissement comme étant provoqué par des forces concentrées dans des régions présentant des irrégularités.

## Zusammenfassung

$T_g$ von Polystyrol wurde durch Copolymerisation mit Acenaphthylen erhöht.    Obwohl die physikalischen Eigenschaften von S20A-Polymerem denen von Polystyrol gleichkommen oder überlegen sind, reduziert der Zusatz von Butadien, Mineralöl oder Isopren zu Poly(styrol-co-acenaphthylen) $T_g$ sehr stark.    Die Herabsetzung von $T_g$ von S20A durch den Zusatz von Butadien war weniger stark, wenn der Zusatz einige Stunden nach Polymerisationsbeginn erfolgte.    Die unverträglichen Terpolymeren waren biegsam, zeigten aber keine Verbesserung der Rissbildungsbeständigkeit.    Als Ursache für die Rissbildungw urden Kräfte angenommen, die in Bereichen mit unregelmässeiger Struktur konzentriert sind.