JOURNAL OF POLYMER SCIENCE VOL. XX, PAGES 485-490 (1956)

Poly-α,β,β-trifluorostyrene*

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INTRODUCTION

Poly-α,β,β-trifluorostyrene is a unique and novel polymer closely related to both polystyrene and polytetrafluoroethylene. It is a high-melting material with fairly low dielectric loss and thus resembles polytetrafluoroethylene. On the other hand, unlike polytetrafluoroethylene, it is soluble in a number of organic solvents. The monomer, α,β,β-trifluorostyrene, was first synthesized by Cohen, Wolosinski, and Scheuer.[1] Using emulsion polymerization techniques, Prober[2] was able to prepare a high polymer in good yield. Very little other than the above has been reported about this interesting material.

RESULTS AND DISCUSSION

Although emulsion polymerization, a radical-catalyzed reaction, gave a high molecular weight polytrifluorostyrene following the method of Prober, no high polymer was isolated when other radical initiators such as benzoyl peroxide, acetyl peroxide, and azobisisobutyronitrile were employed in a large number of experiments, both in bulk and in solution. On attempting ionic polymerization of α,β,β-trifluorostyrene, it was found that, whereas cationic agents like $SnCl_4$ or $TiCl_4$ did not yield any polymer, the anionic agents Na, Na in liquid NH_3, and NaOMe all produced polymer. This is in harmony with a positive character of the double bond to be expected from the substituent fluorine atoms.

Polytrifluorostyrene prepared essentially according to Prober, using dodecylamine hydrochloride as emulsifier and persulfate initiator at 50°C., has a softening point in the neighborhood of 240°C. It dissolves in toluene, chloroform, and methyl ethyl ketone. The rate of swelling is greatest in chloroform and methyl ethyl ketone with a Hildebrand solubility parameter, δ_T, of 9.3 and in other solvents of approximately this value of δ_T. The rate of swelling is also high in pyridine with a δ_T of 10.8, which is evidence of Lewis acid character of the polymer.

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* This work was sponsored by the Signal Corps, Department of the Army.

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Thin films cast from chloroform are clear, tough, and flexible, but thicker specimens exhibit brittle fracture. The x-ray diffraction pattern produced by a beam perpendicular to the plane of a cast film specimen was a diffuse pattern characteristic of amorphous structure. A similar diffraction pattern of a stretched film showed lateral intensification, indicating a marked degree of orientation, but no evidence of crystallization accompanying the orientation. Orientation in the stretched film is also confirmed by high orders of optical birefringence exhibited by the specimen between crossed polarizers.

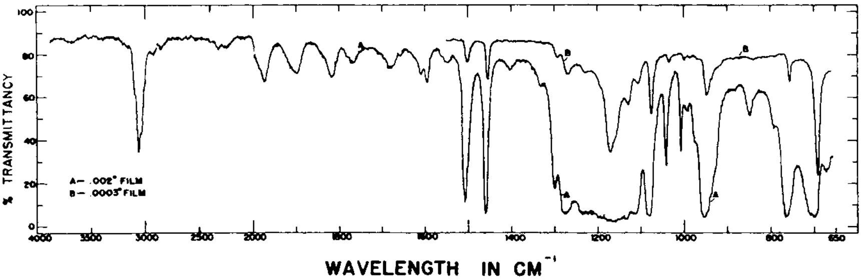

Fig. 1. Infrared absorption spectrum of poly-α,β,β-trifluorostyrene.

The infrared spectrum of polytrifluorostyrene is given in Figure 1. Presence of the aromatic ring is established by the $=$C—H stretching mode at 3060 cm.$^{-1}$ and the skeletal C$=$C in-plane stretching vibrations at 1510 and 1610 cm.$^{-1}$. Monosubstitution of the ring is shown by the characteristic overtone and combination pattern in the region 1650–2000 cm.$^{-1}$ and confirmed by the aromatic CH deformation bands at 690 and 755 cm.$^{-1}$. The 1650–2000 cm.$^{-1}$ bands are seen to be shifted to higher frequencies, which is the usual effect of fluorine in the substituent. The aliphatic CH and CH_2 stretching bands present near 2840 and 2900 cm.$^{-1}$ in polystyrene[3] are absent here. The strong bands at 1075 and at 1175 cm.$^{-1}$ are assigned to CF and CF_2 stretching. These features confirm the structure expected from normal addition polymerization.

The dielectric properties of the washed and dried emulsion polymer were evaluated by the Laboratory for Insulation Research of the Massachusetts Institute of Technology. The polymer is obtained in powder form when it is prepared by emulsion techniques. The dielectric measurements were therefore made both on the powder and on discs prepared by compression molding at temperatures slightly above the softening point. The dielectric constant of the unmolded powder is 2.56 ± 0.05 over the frequency range 10^2 to 10^{11} c.p.s. The variation of loss tangent with frequency is presented graphically in Figure 2, from which it is seen that the polymer is a low loss dielectric material in the specified range. Figure 2 also compares the loss factors of polytrifluorostyrene with polytetrafluoroethylene[4] in this range. (The dielectric constant of polytetrafluoroethylene is 2.09 ± 0.01 throughout.)

At molding temperatures in the vicinity of the softening point, darkening and embrittlement of the polymer were observed to occur, but this did not affect the dielectric properties to any appreciable extent. The dielectric constant of the molded discs was found to be 2.61 ± 0.01 in the frequency range 10^2 to 10^8 c.p.s. The loss tangent varied from 0.0038 to 0.0043 as compared to that of the unmolded powder, which varies from 0.0010 to 0.0033 in the same range. Prolonged exposure of polytrifluorostyrene to heat, however, results in a certain degree of insolubilization accompanying the darkening. A detailed study of the thermal degradation of polytrifluorostyrene has been reported by Madorsky and Strauss.[5]

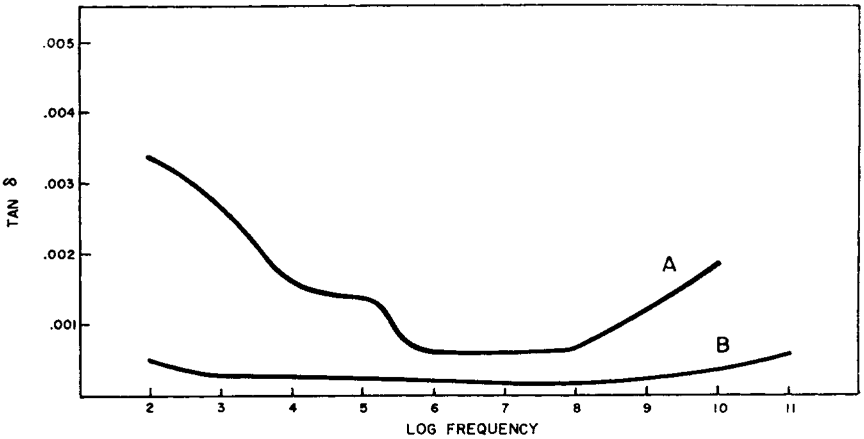

Fig. 2. Dielectric loss factor of polytrifluorostyrene (A) and polytetrafluoroethylene (B).

The mechanical properties of polytrifluorostyrene can be modified by plasticization with the Aroclors (Monsanto Chemical Company) and by copolymerization with styrene or trifluorochloroethylene, which result in considerable lowering of the softening point. The styrene copolymer containing 0.397 mole fraction styrene softens at about 160°C. and that of a trifluorochloroethylene copolymer containing 0.096 mole fraction trifluorochloroethylene at about 195°C. The styrene copolymer was prepared by the usual emulsion polymerization techniques. The copolymerization with trifluorochloroethylene, however, was carried out with some difficulty. Usual emulsion polymerization of an equimolar mixture of trifluorostyrene and trifluorochloroethylene in stainless steel bombs yielded no polymer, but a 3–4% yield of copolymer was obtained when the reaction was carried out in sealed glass tubes for a period of more than 48 hours. Emulsion polymerization of trifluorochloroethylene has been reported to be inhibited by emulsifiers.[6] In view of this, copolymerization with trifluorochloroethylene was carried out without the use of any emulsifying agent, depending upon tumbling action alone to maintain emulsification. The polymer yield was again the same, *ca.* 4%. The halogen analyses (Cl, 2.2%; F, 35.14%) correspond to 0.096 mole fraction of trifluorochloroethylene in the copolymer.

Figure 3 shows the copolymer composition curve of the trifluorostyrene–styrene system. The copolymers were prepared in emulsion at 50°C. The experimental points fit the copolymerization equation using the reactivity ratios $r_1 = 0.070$ and $r_2 = 0.66$, where subscript 1 refers to trifluorostyrene. Using the Price-Alfrey scheme, Q, the reactivity of trifluorostyrene, is calculated to be 0.37 and e, the polarity is +0.95 on the basis of the revised Q and e values of styrene, which are 1.0 and −0.8, respectively. The curve has a crossover at about 0.7 mole fraction of styrene.

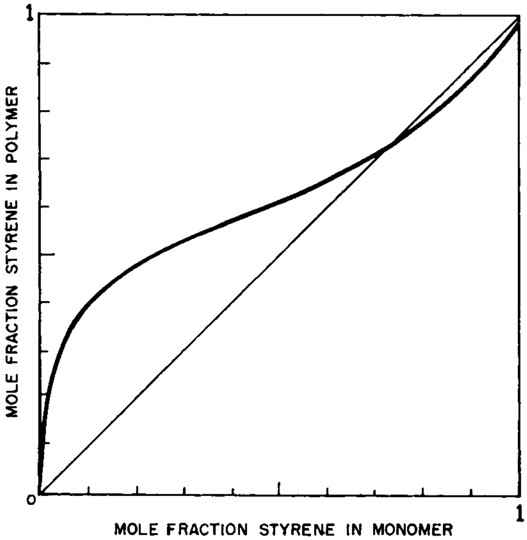

Fig. 3. Copolymerization curve for trifluorostyrene-styrene.

A maximum rate of copolymerization is also found in this region, showing a strong tendency to alternate. As in the ionic polymerization, this behavior is presumed to result from the electron-withdrawing power of fluorine from the double bond.

EXPERIMENTAL

Preparation and Properties of Monomer. α,β,β-Trifluorostyrene monomer was prepared by two methods: (*a*) essentially according to Cohen, Wolosinski, and Scheuer[1] *via* the sequence $CF_2ClCOONa \rightarrow CF_2ClCOCl \rightarrow C_6H_5COCF_2Cl \rightarrow C_6H_5CCl_2CF_2Cl \rightarrow C_6H_5CFClCF_2Cl \rightarrow C_6H_5CF=CF_2$; (*b*) via the alternate sequence $CF_3COCl \rightarrow C_6H_5COCF_3 \rightarrow C_6H_5CCl_2CF_3 \rightarrow C_6H_5CFClCF_3 \rightarrow C_6H_5CF = CF_2$. Method (*a*) with various minor improvements gave an average over-all yield of 21.4%. Method (*b*) was rendered successful when a technique was found for effecting the previously considered difficult removal of ClF. A smooth, exothermic reaction occurs and is complete in ten minutes when the monochloride is heated with acid-washed zinc dust in anhydrous ethylene glycol at 115–120°. Method (*b*) is now the preferred route for many reasons.

The monomer autoxidizes readily (in moist air the final products are benzoic acid and HF) and hence must be protected against any but small amounts of air. The monomer also was found to dimerize readily in a simple thermal reaction, which followed bimolecular kinetics ($k = 0.047$ l. mole^{-1} hr.$^{-1}$ at 100°C., as determined by aid of a refractive index *versus* composition diagram). Consequently, the monomer must be distilled rapidly at a relatively low temperature (b.p. 67.5–68° (75 mm.)) and stored at a low temperature. No observable dimerization is found after several months at -35 to -40°C.

The dimer is an oily liquid, b.p. 132–134° (8 mm.), n_D^{30} 1.4954, d_4^{30} 1.3484.

ANALYSIS: *Calc.:* for $C_{16}H_{10}F_6$: C 60.8; H 3.2; F 36.1. *Found:* C 61.0; H 3.2; F 35.3. MOL. WT. (RAST): *Calc.:* 316. *Found:* 313.

It was inert toward permanganate bromide–bromine reagent, and other oxidizing agents. Its structure is probably 1,2-diphenylhexafluorocyclobutane by analogy with other thermally produced dimers of highly fluorinated ethylenes.[7]

Emulsion Polymerization of Trifluorostyrene. The method was essentially a modification of that of Prober.[3] Freshly distilled trifluorostyrene (159 g.) was polymerized with 960 ml. of aqueous phase containing 20 g. of recrystallized dodecylamine hydrochloride and 1.50 g. of $K_2S_2O_8$ per liter by tumbling in a 50° water bath. After 62 hours of reaction the mixture was coagulated by freezing, and the polymer separated by filtration. The polymer was washed repeatedly with successive portions of hot water and hot methanol until all the emulsifier, residual monomer, and dimer were extracted, and then dried under vacuum at 60°C.

Emulsion Copolymerization of Styrene and Trifluorostyrene. In each run 10 g. of total monomer and 66.7 ml. of aqueous phase containing 10 g./l. dodecylamine hydrochloride and 1.5 g./l. $K_2S_2O_8$ was reacted by tumbling in a 4-oz. bottle under nitrogen at 50°C. The polymer was isolated by pouring the latex into methanol. It was repeatedly washed with hot methanol, twice precipitated from chloroform into methanol, and then dried under vacuum at 50°C.

Emulsion Copolymerization of Trifluorostyrene and Trifluorochloroethylene. A monomer mixture containing 6.5 ml. trifluorostyrene and 4.0 ml. trifluorochloroethylene was sealed in a heavy glass tube with 15 ml. of aqueous phase containing 0.26 g. $Na_2S_2O_8$, 0.12 g. $NaHSO_3$, and 1.0 g. emulsifier and tumbled in a 50°C. water bath for five days. The polymer was isolated by pouring the reaction mixture into excess methanol and purified in the usual manner by precipitating with methanol from toluene solution.

Infrared Spectrum. The infrared spectrum was obtained with a double beam Perkin-Elmer recording spectrophotometer, Model 21.

The authors are indebted to Mr. A. S. Makas for x-ray diffraction, to Miss A. E. Sutton for infrared spectra, to Mr. W. B. Westphal for dielectric measurements, to Drs. E. R. Blout and S. G. Cohen for many helpful discussions, and to Mr. M. W. Kane who prepared most of the monomeric α,β,β-trifluorostyrene.

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Synopsis

An improved preparation and handling procedure for the monomer is described. The polymer was prepared best by emulsion polymerization, although anionic polymerization was also found to be operable. A number of properties of the polymer are described, including solubility, the infrared absorption spectrum, x-ray diffusion (amorphous scattering), dielectric constant (2.56 ± 0.05), and dielectric loss tangent (0.0006 to 0.0035 over the range 10^2 to 10^{11} c.p.s.). Copolymerization with trifluorochloroethylene gave a copolymer containing 0.096 mole fraction of trifluorochloroethylene, and with styrene a copolymer containing 0.397 mole fraction. The copolymerization curve and constants for copolymerization with styrene are presented and discussed.

Résumé

Une préparation améliorée de même qu'une manipulation plus facile ont été décrites pour le monomère. Le polymère est le mieux preparé en émulsion, bien que la polymérisation anionique soit également possible. De nombreuses propriétés du polymère sont décrites, y compris la solubilité, le spectre d'absorption infra-rouge, la diffusion aux rayons-X (diffusion à l'état amorphe), la constante diélectrique (2.56 ± 0.05) et la tangente de perte diélectrique (0.0006 à 0.0035 sur une gamme de 10^2 à 10^{11} c.p.s.). La copolymérisation avec le trifluorochloroéthylène fournit un copolymère contenant 0.096 comme fraction molaire de trifluorochloroéthylène; avec le styrène le copolymère contient 0.397 de ce même monomère. La courbe de copolymérisation et les constantes de copolymérisation avec le styrène sont présentees et soumises à discussion.

Zusammenfassung

Ed wird eine verbesserte Herstellungs- und Behandlungsmethode für das Monomer beschrieben. Das Polymer wurde am besten durch Emulsionspolymerisation hergestellt, trotzdem gefunden wurde, dass anionische Polymerisation auch anwendbar ist. Es werden eine Anzahl Eigenschaften des Polymers beschrieben, unter Einschluss von Löslichkeit, des infraroten Absorptionsspektrums, der Röntgenstrahlen-Diffusion (amorphe Streuung), der dielektrischen Konstante (2,56 ± 0,05) und der dielektrischen Verlust-Tangente (0,0006 bis 0,0035 im Bereich von 10^2 bis 10^{11} c.p.s.). Copolymerisation mit Trifluorochloroäthylen ergab ein Copolymer, welches 0,096 Molfraktionen Trifluorochloroäthylen enthielt, und mit Styrol wurde ein Copolymer erthalten, dass 0,397 Molfraktionen enthielt. Die Copolymerisationskurve und -Konstanten für Copolymerisation mit Styrol werden gegeben und diskutiert.

Received January 24, 1956