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Polyphosphazene Solution-Grown Crystals

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ABSTRACT: Solution-grown crystals of poly[bis(trifluoroethoxy)phosphazene] (PBFP) and poly[bis(2,4-dichlorophenoxy)phosphazene] (PBCP) were prepared from dilute solution by two different procedures. Polymer morphology was studied by transmission and diffraction electron microscopy and by small-angle and wide-angle X-ray diffractometry. Structural modifications have been established for these polymers, where polymorphism depends primarily upon the preparation procedure (solvent) and sample molecular weight. Crystals are relatively thin and consequently some form of chain folding must exist in order to incorporate the macromolecular chain in the crystalline platelets. Dry annealing of polyphosphazene crystals above the first-order thermotropic transition $T(1)$ results in crystal thickening (without void formation), giving rise to a range of thicknesses even within a given crystal, assessed by metal shadowing and measurement. Discrete small-angle periodicities were only observed at temperatures below $T(1)$. A well-defined relationship between crystal thickness was not established previously between $T(1)$ and T_m, the isotropic melting or clearing temperature of PBFP, which is still under further investigation in other polyphosphazenes.

Introduction

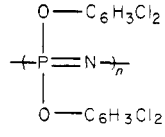
Linear, stable polyphosphazenes were first prepared in the mid-sixties[1,2] even though the first elastomeric material[3] of this type was synthesized before the turn of the century. Today, more than 100 chemically different macromolecules with alternating phosphorus and nitrogen atoms in their skeletal structure are known. Although the variety of these polymers surpasses that of the polysiloxanes, their technological development and applications in the macromolecular hierarchy of materials have been much slower, primarily because of their relatively high cost, batch reproducibility in synthesis,[4] and the long time needed to develop them as stable polymers and copolymers.

The diversity of chemical structures that have evolved recently makes it virtually impossible to characterize more than a fraction of these polyphosphazenes from a fundamental viewpoint and for engineering applications.[5-12] For these flexible[27] mesophase-forming polymers, basic work on the growth and morphology of solution-grown crystals has been sparse and incomplete, even though a better understanding in this area would provide critical information that is basic to dilute solution and to melt processing and fiber-forming operations. Developments in morphology and some structural aspects of polyphosphazenes have developed slowly, presumably because of difficulties associated with the broad molecular weight distribution of most specimens, handling and solvent selection problems in sample preparations, and electron beam sensitivity of these polymers. Still, electron micrographs of crystals have been reported,[16] but without supporting electron diffraction evidence, except in the case of poly(dichlorophosphazene) prepared by the epitaxial polymerization[17] of the cyclohexachloro monomer, where polymorphism was also cited. X-ray diffraction techniques have been used to determine several crystal structures,[18,19] some with varying degrees of uncertainty.[20] Other X-ray data and unit cell information have been mentioned in the literature.[21,22]

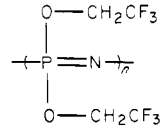
In this paper, we present some unique structural as well as morphological information, some of which was obtained sporadically but systematically, over several years. A combination of X-ray diffraction measurements was made on oriented polymer samples, and electron transmission/diffraction measurements were carried out on solution-grown crystals of poly[bis(trifluoroethoxy)phosphazene] (PBFP) and poly[bis(2,4-dichlorophenoxy)phosphazene] (PBCP) in order to determine their morphology, especially in "single-crystal" form, a factor not established until this time.

Experimental Section

Materials. Unfractionated poly[bis(2,4-dichlorophenoxy)-phosphazene] (PBCP) was kindly provided by Dr. G. Hagnauer of AMMRC, Watertown, MA. Poly[bis(trifluoroethoxy)phosphazene] (PBFP) was obtained from Dr. G. Hagnauer and from



PBCP



PBFP

Professor H. R. Allcock, Chemistry Department, The Pennsylvania State University. A low molecular weight (MW ~ 80 000) and a high molecular weight (MW ~ 500 000) unfractionated PBFP were used in this study. All materials displayed very good elemental analysis and they were readily soluble in several organic

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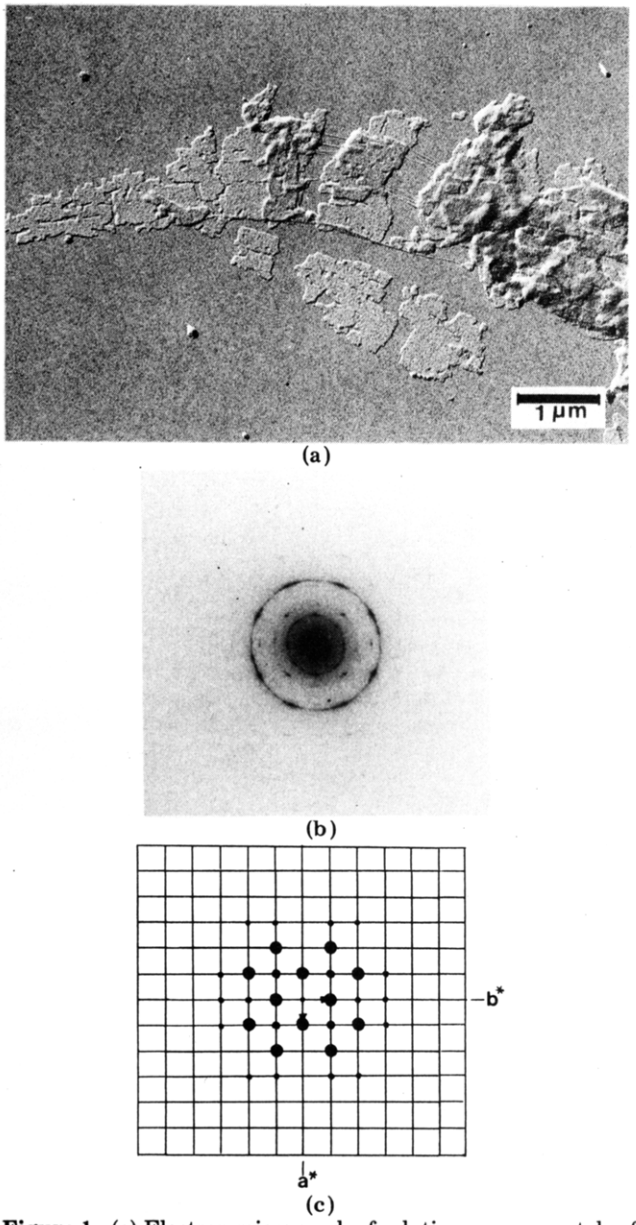


Figure 1. (a) Electron micrograph of solution-grown crystals of high molecular weight poly[bis(trifluoroethoxy)phosphazene] (PBFP) (α-modification). (b) Electron diffraction pattern of PBFP crystals from (a). (c) a^*b^* reciprocal net showing the orthorhombic nature of the unit cell.

solvents despite their relatively broad molecular weight distributions, typically $M_w/M_n \geq 10$.

Solution-Grown Crystals. Two procedures were used to carry out these preparations. The first technique involved forming a 0.03 wt % solution of the polymer in a solvent near its boiling point followed by precipitating the polymer with a nonsolvent.

The other technique was more involved. A carbon-coated Pyrex slide was immersed in a 0.03 wt % polymer solution contained in a long tube and located in a thermostated bath held at the crystallization temperature ±0.1 °C. The partially immersed slide was then withdrawn very slowly by lifting it up on a spool, using a synchronous motor. The linear speed was 0.1–0.2 cm h^{-1}. The procedure[28] will be abbreviated as the dilute solution surface crystallization (DSSC) method. Various morphologies can be obtained by this procedure,[28] which was initially used by Dr. R. D. Patel and one of us (J.H.M.) at the Mellon Institute, Pittsburgh, many years ago.

Oriented Fibers. These were prepared by stretching thin solution-cast films of polyphosphazene at room temperature or, more effectively, by stretching thicker hot-pressed samples held in the vicinity of their $T(1)$ transition or some 30 °C above it when draw ratios as high as ×10 were obtained in several instances.

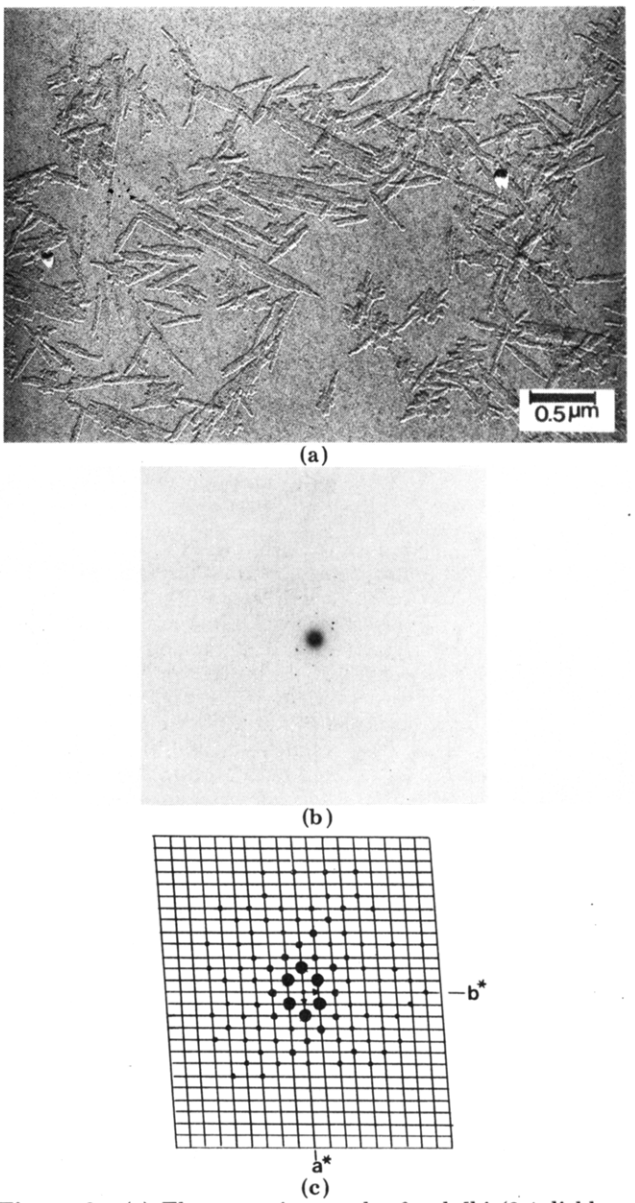


Figure 2. (a) Electron micrograph of poly[bis(2,4-dichlorophenoxy)phosphazene] (PBCP) crystallized from dimethylacetamide solution (approximately 0.03 wt %). (b) Electron diffraction pattern of PBCP crystals. (c) a^*b^* reciprocal net of these crystals.

Results and Discussion

Crystal Morphology. Specifically, crystals of high molecular weight PBFP in Figure 1a were prepared from tetrahydrofuran (THF), using a hot solution of 0.03 wt % of the polymer and then precipitating the PBFP crystals with xylene. Figure 1b illustrates the diffraction pattern, and its corresponding a^*b^* reciprocal lattice net is depicted in Figure 1c. From drawn fibers of PBFP and the crystal data the orthorhombic unit cell of the α-modification of PBFP was found to have the following dimensions: a = 10.16, b = 9.35, and c = 4.86 Å. Other polymorphs have been found, too.[23] The crystals shown here are about 130 Å thick. Dimensions were deduced by using the standard metal shadowing procedures.

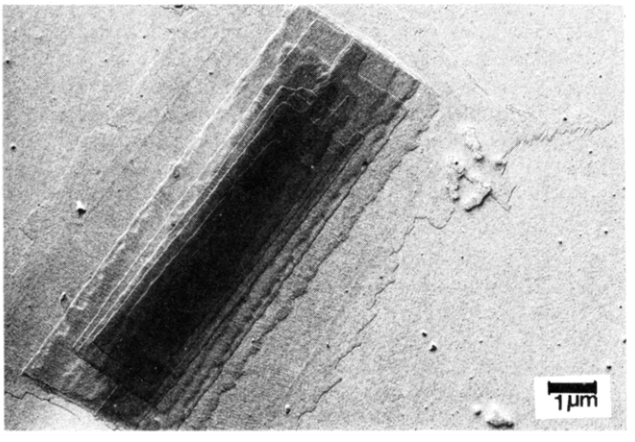
PBCP crystals (Figure 2a) were prepared from a dimethylacetamide solution. The crystals were typically 1 μm long and 0.05–0.1 μm wide with a thickness of 40–60 Å, depending upon the preparation procedure. Figure 2b illustrates the diffraction pattern, and Figure 2c shows the corresponding a^*b^* reciprocal lattice net of the monoclinic structure. From oriented fiber X-ray patterns and this electron diffraction information, the unit cell dimensions

were deduced to be a = 21.6 Å, b = 16.5 Å, and c = 4.86 Å, with γ = 94°.

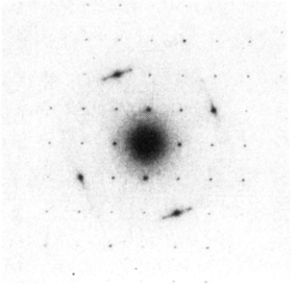
The morphology of low molecular weight PBFP crystals (β-modification)[23] prepared by this method is shown in Figure 3a along with the diffraction pattern in Figure 3b. Comparable-quality solution-grown crystals were obtained by using the carbon-coated slide extraction procedure (DSSC) mentioned above. Note that there is a "rim" around these rectangular-shaped crystals, which are well developed and structurally comparable with the square-like habits of Figure 4a.

Polymorphism in polyphosphazenes depends primarily upon the preparation procedures (solvent and heat treatment) and sample molecular weight. Since the crystals are fairly thin in these polymers, which are all of relatively high molecular weights, some form of chain folding exists in these solution-grown crystals. In the thermotropic state there has not been a clear solution to the $T(1)$ morphology until now.

Crystal Annealing. A series of annealing experiments conducted on low molecular weight PBFP crystals (β-modification) provides some unique morphologies before and after annealing in the thermotropic state. Figure 4 shows a series of micrographs obtained after heat treatment at (b) 70 °C for 30 min, (c) 150 °C for 30 min, and (d) 200 °C for 30 min in a nitrogen environment in order to prevent degradation. Inspection of these micrographs clearly shows that an erratic thickening and concomitant surface roughening of the crystals (prepared at room tempeature) takes place above the $T(1)$ transition of 85–90 °C, as illustrated in Figures 4 and 5. Another micrograph (Figure 5) depicts an annealed high molecular weight PBFP (α-modification) crystal that was heat treated in nitrogen at 150 °C for 30 min before shadowing at room temperature. The irregularity or roughness is more pronounced in this example and is in keeping with other ob-

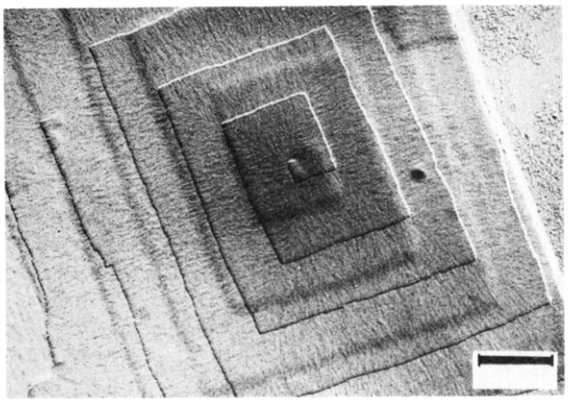


(a)

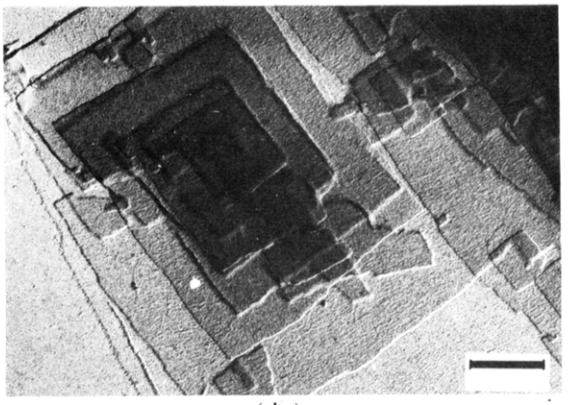


(b)

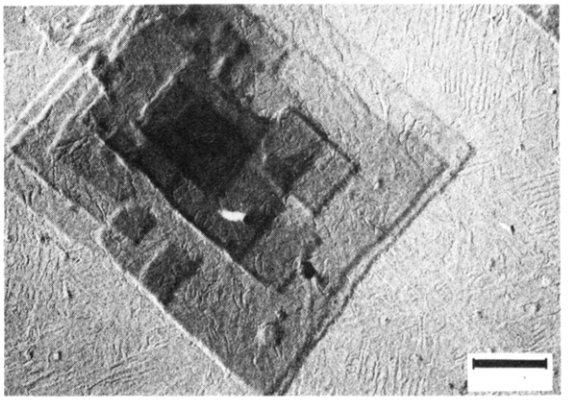
Figure 3. (a) Electron micrograph of PBFP crystals (β-modification) obtained by the dilute solution surface crystallization (DSSC) procedure. (b) Diffraction pattern from sample in (a).



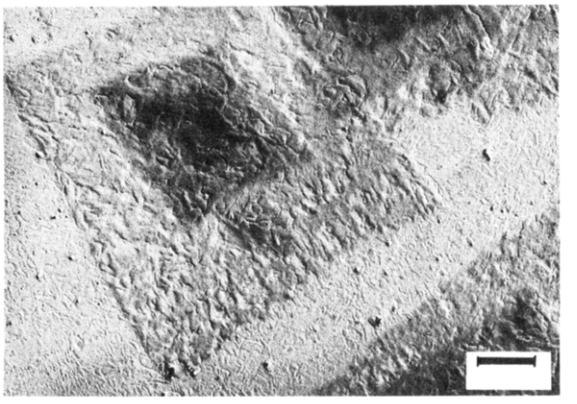
(a)



(b)



(c)



(d)

Figure 4. (a) Electron micrograph of solution-grown crystals of PBFP (β-modification). (b) Electron micrograph of crystals after annealing at 70 °C for 30 min. (c) Electron micrograph of crystals after annealing at 150 °C for 30 min. (d) Electron micrograph of crystals after annealing at 200 °C for 30 min.

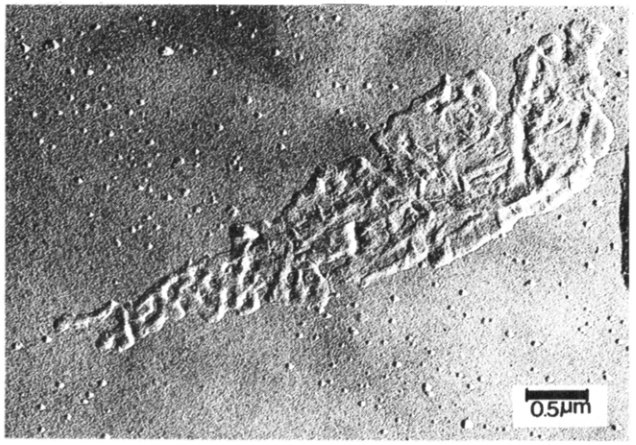


Figure 5. Electron micrograph of high molecular weight PBFP (α-modification) annealed at 150 °C for 30 min. Note the erratic thickening over the entire crystal.

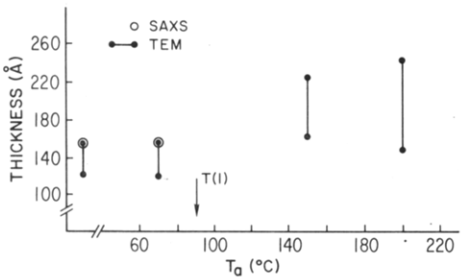


Figure 6. (a) Crystal thickness of PBFP specimens (Figure 4) assessed by transmission electron microscopy using metal shadowing (●). (⊙) Long period of PBFP single-crystal mats after annealing below $T(1)$. No discrete small-angle scattering was noted after annealing at temperatures above $T(1)$.

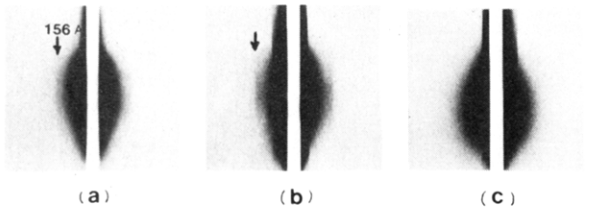


Figure 7. (a–c) Small-angle X-ray diagrams of low molecular weight PBFP crystal mats corresponding to the samples in Figure 4a–c, respectively.

servations (Figure 4 of lower molecular weight). Supporting evidence is obtained from annealed crystal mats. Below $T(1)$ no increase in long period takes place, but substantial crystal thickening or internal disordering occurs at temperatures above $T(1)$, where discrete SAXS scattering is absent (see results in Figure 6). Small-angle diagrams (Figure 7) only show a single sharp reflection for samples annealed below $T(1)$.[29]

This evidence must mean either that fluctuations in the chain direction above $T(1)$ arise from anisotropic nematic-like domains or that discrete periodicities are too large to be recorded (i.e., too close to the beam stop). In any case, chain mobilization accompanying thickening can only take place at or above $T(1)$. It is also in this regime that property enhancement (such as orientation) can be brought about through stretching[10] the polymer(s) in this temperature regime.

It is interesting to compare the morphologies of high and low molecular weight PBFP crystals even though all samples have broad molecular weight distributions. Figure 1a shows fibrillar connections occurring in the [a] direction

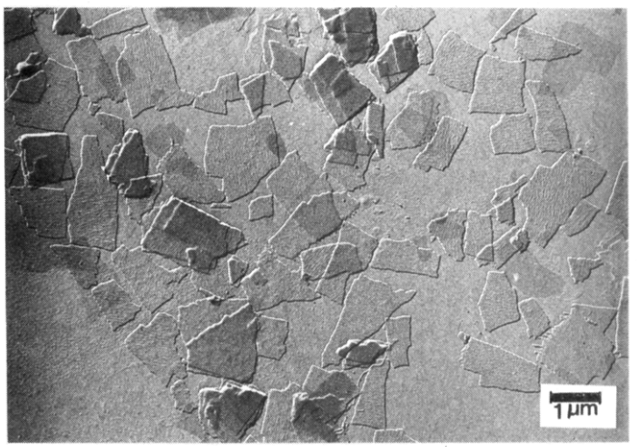


Figure 8. Low molecular weight ($M_n \sim 80\,000$) PBFP-type crystal (β-modification) after some dispersion in methanol (a nonsolvent) at room temperature.

within fractured crystalline regions, whereas fragments of the lower molecular weight PBFP (Figure 8) are everywhere devoid of visible connections. More work is required in this area.

It is important to distinguish between the behavior of solution-cast polymer films, which are ductile, and films annealed above $T(1)$, which are brittle. Similarly, melt-crystallized PBFP is brittle and no discrete SAXS pattern is found, in accord with an extended chain but not necessarily a fully extended chain morphology (as yet we have no evidence for the latter structure). Still, the development of anisotropic domains of superstructure must occur in flexible-chain polyphospazenes even though the glass transition temperature is low (approximately –66 °C in the case of PBFP.

Polyphosphazene crystals have been recently classified as condis crystals[24] since they exhibit relatively large configurational entropies on passing through $T(1)$ and therefore differ in this respect from the more conventional rigid rod polymers,[14,15] plastic-type crystals, or small-molecular liquid crystals (see, for example, ref 24). Even so, there is still some question as to the exact magnitude of the enthalpy of the condis crystal melting itself.[24] Some of the problems may well mimic in some respects the phase behavior reported recently in other polyesters,[26] but more details are required in polyesters where morphological data are sparse. Still, it is apparent from the current work on polyphosphazenes that thickening is directly and indirectly observed upon annealing and that disorder prevails at temperatures above $T(1)$. Upon cooling to room temperature, hexagonal and chain-extended orthorhombic crystal modifications often persist together.

Conclusions

1. Solution-grown crystals of PBFP and PBCP form chain-folded crystals from dilute solution.
2. Polymorphic crystalline forms occur in PBFP polyphosphazenes.
3. Whenever PBFP crystals are heat treated below $T(1)$, no crystal thickening takes place, but at annealing temperatures above $T(1)$ but below T_m, erratic thickening occurs, as chain extension takes place.

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(27) As opposed to stiff rodlike molecules which unequivocally exhibit liquid crystal properties above some critical concentration.[13-15]
(28) Presently we are trying to model this crystallization process.
(29) It has been established by J. H. Magill, J. S. Lin, and J. M. Schultz (unpublished) that PBFP shows no discrete reflection above the $T(1)$ transition whenever bulk polymer is measured at 120 °C (i.e., above $T(1)$) (work conducted at Oak Ridge SAXS laboratory).

Polymerization Behavior of *p*-Quinone Bis(benzenesulfonimide) as an Acceptor Monomer

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ABSTRACT: The electron affinity of *p*-quinone bis(benzenesulfonimide) (QBS) was estimated from the charge-transfer band between QBS and hexamethylbenzene to be 2.17 eV. QBS was found to copolymerize alternatingly with styrene (St), acenaphthylene, *n*-butyl vinyl ether, isobutyl vinyl ether, 2-chloroethyl vinyl ether, and phenyl vinyl ether in benzene at 60 °C in the presence of α,α'-azobis(isobutyronitrile) (AIBN). However, QBS and vinyl acetate gave no polymeric product. Studies of terpolymerizations of the QBS–maleic anhydride (MAnh)–St, QBS–*p*-chloranil (PCA)–St, QBS–7,7,8,8-tetrakis(methoxycarbonyl)quinodimethane (TMCQ)–St, and QBS–7,7,8,8-tetracyanoquinodimethane (TCNQ)–St systems afforded the relative reactivity of the St complexes toward the polymer radical with the QBS–St complex terminal unit to be MAnh–St complex (1/30) < PCA–St complex (1/5) < TMCQ–St complex (1/1.18) < QBS–St complex (1) < TCNQ–St complex (1/0.01). This order, except for the PCA–St complex, follows that of the electron-accepting character of the acceptor monomers. Influence of the exocyclic heteroatom was discussed on the basis of the unusual reactivity, PCA–St complex exhibiting a much lower reactivity in comparison with the electron-accepting character of PCA.

Unsubstituted quinodimethane[1] is so reactive that it cannot be prepared as the monomer unless the reaction is carried out at −78 °C in toluene at very dilute concentration; otherwise it reacts immediately to give its polymer. Electron-accepting quinodimethane compounds with strong electron-withdrawing substituents become much less reactive and can be synthesized under ordinary conditions as crystalline materials, e.g., 7,7,8,8-tetracyanoquinodimethane (TCNQ),[2] 7,7,8,8-tetrakis(methoxycarbonyl)quinodimethane (TMCQ),[2] 7,7,8,8-tetrakis(ethylsulfonyl)quinodimethane,[3] and so on, and they are polymerizable as acceptor monomer.[3-5] Furthermore, *p*-benzoquinone is a stable, yellow, crystalline, electron-accepting compound and is conventionally useful as an inhibitor[6,7] and a retarder[8] for free radical polymerization. As one of various reaction paths[9] to account for this inhibition reaction, alkylation on both oxygens of *p*-benzoquinone was proposed to take place to yield ether bonding, implying a copolymerization of *p*-benzoquinone with monomers. Stronger electron-accepting *p*-benzoquinones with electron-withdrawing substituents such as *p*-chloranil (PCA) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) are subject to copolymerization with a donor monomer in a more definite fashion as acceptor monomer.[10-13] Quinine diimine, prepared as a colorless crystalline compound by Willstätter and Mayer,[14] is expected to be an intermediate compound between *p*-benzoquinone and quinodimethane from the relationship of Coppinger and Bauer[15] between the stability of hetero *p*-benzoquiones and the electronegativity of their exocyclic atoms, carbon (2.50),[16] nitrogen (3.07),[16] and oxygen (3.50).[16] Unsubstituted *p*-quinone diimine is very susceptible to light and acid, especially in solution, and may undergo reactions such as hydrolysis and polymerization.[17] Adams and Nagarkatti[17] reported that *p*-quinone diimines carrying electron-withdrawing substituents such as acyl, alkylsulfonyl, and acrylsulfonyl groups at exocyclic nitrogen atoms become less susceptible to hydrolysis, being likely more convenient for studies of polymerization. The polymerization behavior of the quinone imides has rarely been

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