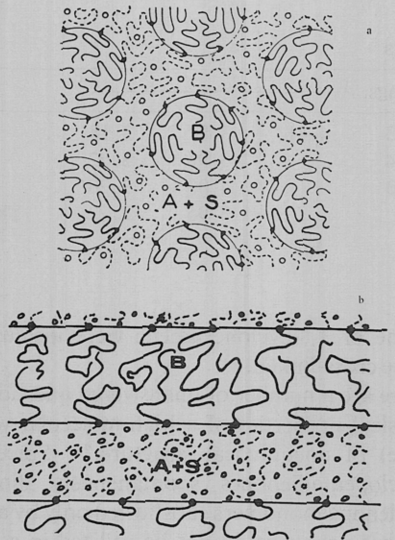

Figure 2. (a) Sections of a hexagonal packing of cylinders normal to the plane of the figure. (b) Section of lamellae structure normal to the plane of the figure.

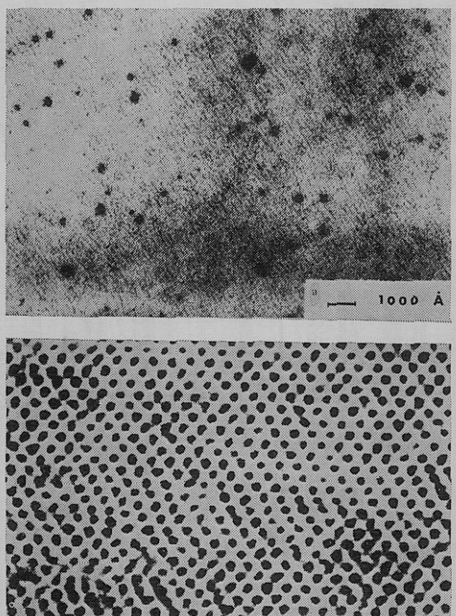

Figure 3. Electron micrographs of three types of structures: (a) (A–B)S, where A is polyisoprene ($M = 24{,}500$), B is poly(vinylpyridine) ($M = 40{,}500$), S is 99% poly(methyl methacrylate) (pmma) (the black spots are formed by isoprene aggregates in the pmma matrix); (b) (A–B)S, where A is polystyrene ($M = 49{,}000$), B is polybutadiene ($M = 12{,}400$), S is 30% pmma (the black spots are the perpendicular sections of a hexagonal packing of polybutadiene cylinders); (c) (A–B)S, where A is polyisoprene ($M = 55{,}000$), B is poly(vinyl-2-pyridine) ($M = 45{,}000$), S is 21% poly(vinyl acetate) (the black stripes are the sections, normal to their planes, of the parallel layers formed by polyisoprene).

All of these materials are viscous fluids which are difficult to handle and presumably of little practical interest. However, their properties can be drastically changed by using liquid monomer as a solvent which is polymerized eventually,[3,11] *e.g.*, by uv irradiation. Thus, by this method, one obtains a *rigid* material which retains the periodic structure of the original liquid, as may be seen from the electron microscope photographs (Figure 3)[12] obtained from thin cuttings (500 Å) stained with osmium tetroxide.

As shown by low-angle X-ray diffraction, the polymerization technique changes the structural parameters of the original gel only slightly. In addition, this procedure permits us to see by electron microscopy the aggregates which cannot be investigated by X-ray diffraction (see Figure 3a).

Two final remarks may be of some interest. (1) It is possible to use as a solvent S the same monomer which produces the soluble block sequences. We then obtain a material containing only two kinds of polymers, A and B. (2) In the limiting case, when the concentration of S approaches zero, we have the pure organized copolymer that we have described above. It has been studied by other authors.[9–13]

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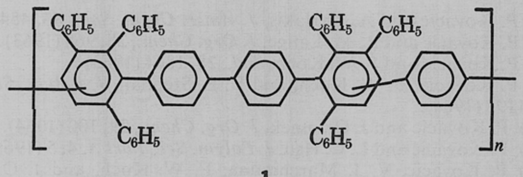
Received March 8, 1971

Poly(*p*-phenylene)

High-molecular-weight phenylated polyphenylenes obtained from the 1,4-cycloaddition reaction of biscyclopentadienones or bispyrones with bisacetylenes[1–5] have properties which are quite different from those of unsubstituted polyphenylenes prepared by other methods. The phenylated polyphenylene **1**, in which the phenylated rings have a 1:1 para to meta catenation ratio and have number-average molecular weights of 40,000–100,000, are light yellow, amorphous, and completely soluble in common organic solvents (benzene, chloroform, etc.) in concentrations of up to 10 wt %.



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By contrast, those polyphenylenes prepared either from benzene by a Friedel–Crafts reaction under oxidative condi-

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TABLE I
d SPACINGS AND POLYPHENYLENES

	d spacings, Å							Ref
p-Quaterphenyl			4.63	4.53	4.41	3.87	3.18	*a*
Poly(*p*-phenylene) (1,3-cyclohexadiene)	9.07	6.39		4.54		3.96	3.22	13
Poly(*p*-phenylene) (benzene)				4.53		4.00	3.20	6
Poly(*p*-phenylene) (1,4 cycloaddition)			4.60			3.95	3.22	This work

[a] C. J. Toussaint and G. Vos, *J. Chem. Soc. B*, 813 (1966).

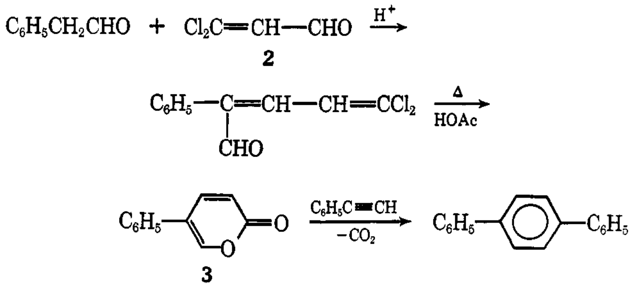
tions[6-12] or the 1,4 polymerization of 1,3-cyclohexadiene followed by dehydrogenation[13-16] are brown to black, crystalline, and insoluble in any solvents.

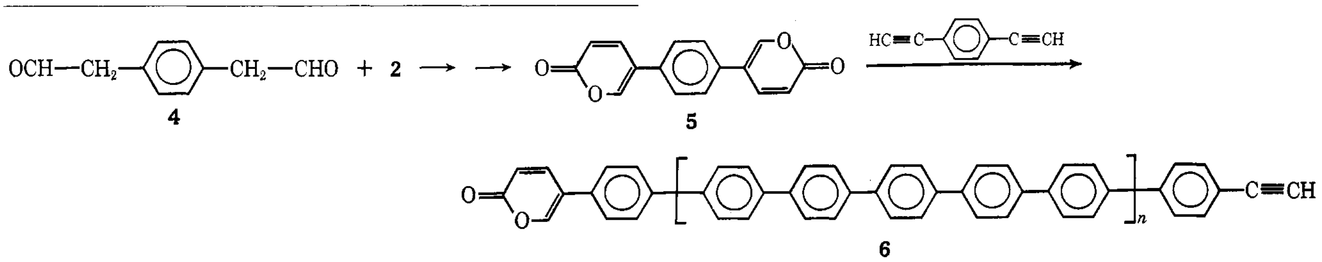
The λ_{max} for poly(*p*-phenylene) calculated by Kuhn's root law[17] is 343.8 nm, while calculations using other equations in combination with experimental data obtained from oligomeric phenyls show that λ_{max} approaches a limiting value of 339 nm as the degree of polymerization becomes infinite.[18-21] Although the phenylated polyphenylenes were light yellow and showed broad maxima near 340 nm, these polymers might be expected to exhibit a low λ_{max} since the pendant phenyl groups would offer steric hindrance to the copolanar excited state. Experimental values as high as 395 nm have been reported,[11] however, for polyphenylenes prepared from benzene. The problem of whether this absorption actually can be attributed to the presence of conjugated *p*-phenylene or to *p*-quinoid-type linkages[11,22] has not been resolved.

Oligomeric para phenyls are either very difficulty soluble or insoluble crystalline materials, yet substitution on the ring markedly improves their solubilities.[23] For example, although *p*-octaphenyl is insoluble and high melting (>500°), octamethyl-*p*-octaphenyl is soluble to the extent of 13 g/l., and with mp = 254°. We had attributed the lack of crystallinity and thus the good solubility of the phenylated polyphenylene **1** to the pendent phenyl groups, yet there was still some doubt as to whether the poly(*p*-phenylenes) prepared from benzene or 1,3-cyclohexadiene were insoluble because they might be cross-linked.

Thus, there are a number of unanswered questions concerning the physical properties of a high-molecular-weight poly(*p*-phenylene) of unequivocal structure.[24] Since monosubstituted cyclopentadienones spontaneously dimerize, biscyclopentadienone monomers substituted only by a connecting para phenylene group could not be utilized in a similar 1,4-cycloaddition synthesis of unsubstituted polyphenylenes. Certain monosubstituted α-pyrones, however, are stable in their monomeric form and react with acetylenes to form benzene derivatives.[25]

The synthesis of 5-phenylpyrone (**3**) was effected by the reaction of phenylacetaldehyde with dichloroacrolein (**2**) followed by cyclization.[26] Although the reaction of 5-phenylpyrone with phenylacetylene could be expected to afford both *m*- and *p*-terphenyl, fortunately, a quantitative yield of *p*-terphenyl was obtained exclusively, as shown by comparison with an authentic sample. This isomer was the one predicted by the extended Hückel MO calculations of the net charge distribution on the reactants.[27]





Similarly, the reaction of *p*-phenylenebisacetaldehyde[28] (**4**) with **2**, followed by cyclization, afforded the *p*-phenylenebispyrone **5**. Reaction of **5** with *p*-diethynylbenzene in 1,2,4-trichlorobenzene at 250° (sealed tube) afforded a quantitative yield of poly(*p*-phenylene) (**6**) which had precipitated from the reaction solvent.

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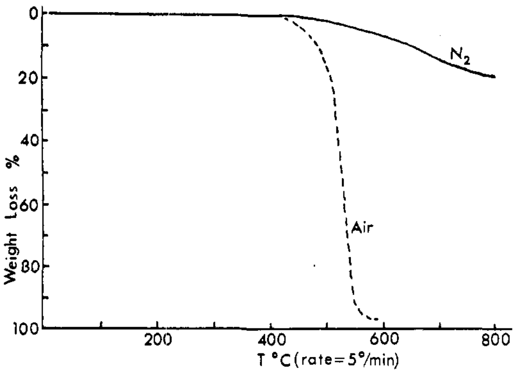

Figure 1.

This poly(*p*-phenylene) was extremely difficult to burn in order to obtain an elemental analysis; however, the lower limit of molecular weight by carbon analysis is an undecaphenyl, $n = 2$. (*Anal.* Calcd for **6**, $n = 2$: C, 91.59. Found: C, 91.20.) The infrared spectrum showed only a very weak carbonyl absorption (pyrone and/or carboxylic acid) and a strong C–H out-of-plane deformation characteristic of the *p*-phenylene moiety at 800 cm^{-1}. It has been claimed[6] that an increasing degree of para phenylation leads to a shift of this frequency to lower wavelengths,[29] and for this reason the polyphenyls prepared from 1,3-cyclohexadiene (811 cm^{-1}) have lower molecular weights than those prepared by benzene polymerization (802–807 cm^{-1}). If this interpretation is correct, the *p*-polyphenylenes prepared by this 1,4 cycloaddition have the highest molecular weight.

Poly(*p*-phenylene) (**6**) was insoluble in all solvents and was crystalline, showing d spacings characteristic of *p*-quaterphenyl and poly(*p*-phenylene) obtained from 1,3-cyclohexadiene and benzene (Table I).

By contrast to those poly(*p*-phenylenes) prepared by other methods, the polymer **6**, obtained from the 1,4 cycloaddition, was yellow with $\lambda_{\max(\text{refl})} = 340$ nm, more in agreement with the theroetical value.[17–21]

Finally, we observed that whereas the phenylated polyphenylenes (**1**) had a break in the tga at 550° in air and decomposed rapidly, they lost about 30–35% of their weight rather sharply under a nitrogen atmosphere at about 550°; we had attributed this to the loss of some of the pendant phenyl groups.[1] The tga analysis of poly(*p*-phenylene) (Figure 1) reinforces this interpretation in that although a similar decomposition (tga ~ 500°) of **6** in air is observed, under nitrogen, **6** loses 10% of its weight at 650° and only 20% at 800°.

Thus, poly(*p*-phenylene) is indeed a highly crystalline, insoluble, thermally stable polymer, but is not highly colored.

Acknowledgment. This research was supported in part by the U. S. Army Research Office, Durham, N. C. The authors wish to acknowledge the assistance of Mr. L. Stoel in obtaining the reflectance spectra, Dr. N. C. Baenziger for the X-ray data, Mr. L. Mathias for the tga, and Mr. G. K. Noren for assistance.

(29) *p*-Quaterphenyl, *p*-pentaphenyl, and *p*-sexiphenyl show bands at 825, 818, and 812 cm^{-1}, respectively.

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Received January 8, 1971

Electron Microscopy of Poly(vinyl chloride) and Ethylene–Vinyl Acetate Rubber Systems

Commercially available rubber-modified plastics such as ABS polymers generally contain unsaturated rubbers. Attempts to utilize saturated rubbers for obtaining better weatherability characteristics have been conducted in many laboratories. One of the interesting systems is a graft copolymer composed of poly(vinyl chloride) (PVC) and ethylene–vinyl acetate rubber (EVAc).

For the electron microscopic observation of the micromorphology of rubber-modified plastics having unsaturated rubbers, Kato's osmium tetroxide (OsO_4) procedure[1] has been effective. However, this technique is not applicable to the PVC–EVAc system, because neither the PVC nor the EVAc phase is susceptible to the staining agent, OsO_4.

In the present study attempts have been made to overcome this staining difficulty of PVC–EVAc systems by introducing an additional treatment before the application of Kato's method.

Materials. The PVC and EVAc used in the present study were Geon 103EP8 (DP ≈ 800) manufactured by the Japanese Geon Co. and Levaplene-450 supplied by Fabenfabriken Bayer AG. PVC–EVAc systems were prepared by blending and grafting. The blending was carried out by milling a mixture of a formulated PVC powder and EVAc pellets on an 8-in. open roll at 155° for 6 min. Then the resulting 1-mm thick sheets were compression molded at 160°. The grafts, on the other hand, were prepared by dissolving EVAc in vinyl chloride monomer, followed by normal suspension polymerization of the monomer. The composition of PVC–EVAc was varied from 5/95 to 90/10 for the blends and from 5/95 to 50/50 for the grafts.

EVAc Staining Procedure. A specimen block with suitable dimensions for ultramicrotomy was placed in methanol saturated with sodium hydroxide. The solution was heated to boiling and refluxed for 1–2 hr. The specimen was then taken out, washed with water, and dried. The procedure employed thereafter was the same as Kato's method: the specimen was exposed to OsO_4 vapor for about a week and subjected to ultrathin sectioning.

By the treatment mentioned above, it is believed that the acetate groups in the EVAc near the specimen surface were saponified to hydroxy groups, as evidenced by complete disappearance of the C=O band (~1725 cm^{-1}) and an increased intensity of the OH band (~3300 cm^{-1}) in the atr infrared trace (Figure 1). Hydroxyl groups are capable of

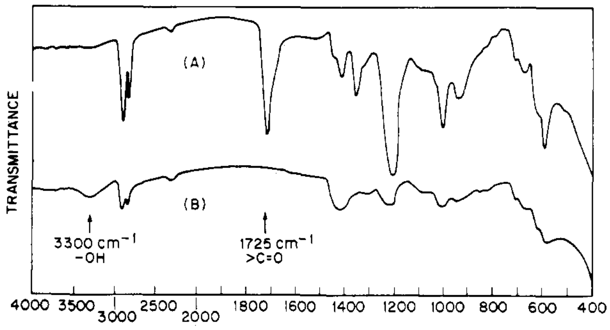

Figure 1. Atr infrared spectra of a PVC–EVAc = 70/30 graft system before (top) and after (bottom) treatment with methanol saturated with sodium hydroxide.

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