would alter the apparent value of $\bar{A}_w/\bar{A}_n$ obtained by gpc in opposite directions. It is not possible to predict which effect would predominate from the data at hand. Branching might also be expected to lead to species more susceptible to degradation, but we have no specific evidence on this point.[16]

---

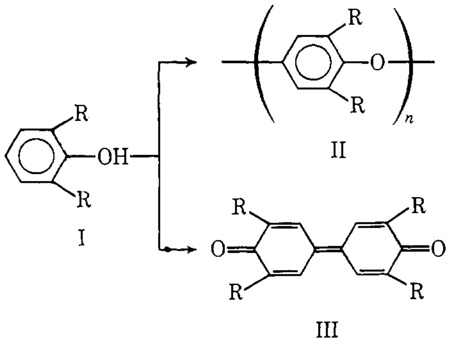
(16) See also V. V. Korshak, *Dokl. Akad. Nauk SSSR*, **64**, 525 (1949).

Acknowledgment. Support of this work by the National Science Foundation under Grant No. GP-5349 is gratefully acknowledged. The work was performed in the Materials Research Center Laboratory, Rensselaer Polytechnic Institute, a facility supported by the National Aeronautics and Space Administration, and is taken from the M.Sc. thesis of Ilan Katz. We wish to thank S. Y. Hobbs and R. N. Kelley for assistance in the measurements.

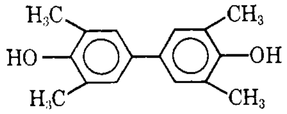
Communications to the Editor

Poly(2,6-diphenyl-1,4-phenylene oxide)

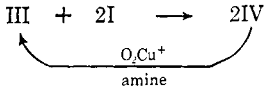
The oxidative polymerization of 2,6-disubstituted phenols with oxygen in the presence of amine complexes of copper(I) salts as catalysts has been shown to yield aromatic polyethers (II) or diphenoquinones (III) as products.[1,2] It has also been shown that by increasing the size of the substituents, R, diphenoquinone formation is favored.[3] It has been further demonstrated in the oxidation of 2,6-dimethylphenol that increasing the temperature of the reaction also increases the amount of diphenoquinone formed.[4] In fact by raising the reaction temperature from 25 to 100° the reaction changes from one that gives predominantly C–O coupling to one that gives predominantly C–C coupling. Endres[4] has suggested that this behavior may be due to the presence of at least two catalytic species in the reaction, one of which favors C–O coupling and the other C–C coupling and that the latter predominates at high temperatures.



We subsequently found that tetramethyldiphenoquinone reacts very rapidly with 2,6-dimethylphenol at 100° in the presence of amines to give predominantly (85%) the C–C coupled product (IV).[5] Hence, in the polymerization of 2,6-dimethylphenol at elevated temperatures the predominant reaction becomes



IV



$$\text{III} + 2\text{I} \longrightarrow 2\text{IV}$$

Oxidation of 2,6-diphenylphenol[6] with oxygen in pyridine solution at room temperature using copper(I) chloride as catalyst yields as product only low molecular weight polymer as well as substantial amounts (∼50%) of the diphenoquinone. An examination of molecular models indicated that it should be feasible to prepare high molecular weight poly(2,6-diphenyl-1,4-phenylene oxide) (II, R = phenyl); therefore this problem was examined further.

We have found that the most active catalysts for oxidative coupling reactions are obtained by using bidentate amines such as N,N,N′,N′-tetramethylethylenediamine (TMEDA) as ligands for the catalyst;[2,7] hence, this class of catalysts was examined for the oxidative polymerization of 2,6-diphenylphenol.

At 30° with a catalyst consisting of equimolar amounts of copper(I) chloride or copper(I) bromide and TMEDA as catalyst only polymers with low intrinsic viscosities (∼0.1 dec/g in CHCl$_3$ at 25°) were obtained. Surprisingly, in contrast to our experience with oxidative polymerization of 2,6-dimethylphenol, as the temperature of the reaction mixture was raised polymers with higher intrinsic viscosities were obtained and above 60° high molecular weight polymers were readily obtained with only small amounts of the diphenoquinone as a by-product. An example of the polymerization of 2,6-diphenylphenol follows.

To a 250-ml wide-mouthed erlenmeyer flask equipped

---

(1) A. S. Hay, H. S. Blanchard, G. F., Endres, and J. W. Eustance, *J. Amer. Chem. Soc.*, **81**, 6335 (1959).

(2) A. S. Hay, *Advan. Polym. Sci.*, **4**, 496 (1967).

(3) A. S. Hay, *J. Polym. Sci.*, **58**, 581 (1962).

(4) G. F. Endres, A. S. Hay, and J. W. Eustance, *J. Org. Chem.*, **28**, 1300 (1963).

(5) A. S. Hay, *Tetrahedron Lett.*, 4241 (1965).

(6) J. Plesek, *Chem. Listy*, **50**, 252 (1956).

(7) A. S. Hay, *J. Org. Chem.*, **27**, 3320 (1962).

with a Vibromixer stirrer, oxygen inlet tube and a thermometer in a bath at 85° was added 100 ml of *o*-dichlorobenzene. Oxygen was passed through (500 ml/min) the vigorously stirred solution and over a 1 hr period there was added dropwise a solution consisting of 30 g (0.12 mol) of 2,6-diphenylphenol, 0.28 g (0.002 mol) of copper(I) bromide and 0.23 g (0.002 mol) of TMEDA dissolved in 40 ml of *o*-dichlorobenzene (under N_2). After a further 100 min the reaction mixture was very viscous. The polymer was isolated by adding the reaction mixture dropwise to 500 ml of methanol, to which was added 5 ml of concentrated hydrochloric acid and 5 ml of hypophosphorous acid, and removed by filtration. The precipitate was dissolved in 250 ml of chloroform filtered through Celite, and reprecipitated by dropwise addition of 750 ml of methanol. The almost colorless polymer was removed by filtration and dried *in vacuo* (15 mm) at 100° for 6 hr. There was obtained 28.3 g (0.116 mol, 93% yield) of polymer with $[\eta] = 0.58$; $\bar{M}_n = 150{,}000$, $\bar{M}_w = 296{,}000$.

Anal. Calcd for $C_{18}H_{12}O$: C, 88.50; H, 4.95. Found: C, 88.62, 88.31; H, 4.85, 5.01.

The polymer has a glass transition at 230° and above the glass transition temperature it rapidly crystallized and then melts at approximately 480°. Thermogravimetric analysis (300°/hr) indicates the polymer is thermally stable up to 520°; in nitrogen and in air it begins to lose weight at 430°.

Further details will be published in a subsequent paper.

Allan S. Hay
General Electric Research and Development Center, Bldg, K-1
Schenectady, New York 12301

Received October 28, 1968

Spontaneous Catalyst Fracture and Its Influence on Nascent Polyethylene Morphology

Previously, we have described a way to produce nascent polyethylene films from vanadium based Ziegler-Natta polymerization catalyst anchored on various substrates which were immersed in nonsolvent media for polyethylene.[1] The mechanical properties and consequently the inherent morphology of these films vary widely depending upon the polymerization conditions and catalyst deposition. A direct electron microscopic observation of these films reveals that their texture is constituted of a great number of small polyps in the range of 1000 Å diameter, bonded together by a network of ribbons. According to the polymerization conditions, the texture can be described in some cases as essentially "polyplike" leading to almost no mechanical strength while in other cases a significant network of ribbons has developed during the polymerization, linking polyps together and imparting an increased tensile and tear strength to the film. Figure 1 is a combination of these two cases and illustrates a texture showing various size ribbons emerging from a matrix of polyps. The relationship between these observations and those reported by other authors also studying the structure of nascent polyolefins does not appear straightforward on first examination but they are probably reconcilable. In the case of polypropylene grown on large crystals of α-$TiCl_3$, the initial structure of the nascent polymer is essentially polyplike[2] even though recent evidence[3] tends to favor a "whiskerlike" structure in later phases of polymerization. In other cases, and particularly with polyethylene,[4,5] the structure of the nascent polymer is described as fibrillar, which probably can be related to the ribbons that are observed on Figure 1.

In order to understand why such a variety of structures are found, a number of experiments were performed wherein nascent polyethylene films were prepared under a variety of conditions, with rate of polymerization varying several hundredfold. In all cases the catalyst was support-anchored crystalline VCl_3, while the cocatalyst was $AlEt_3$. Polyps were found even after a few seconds of polymerization and originated from polymer coating of catalyst crystals or fragments thereof. This phenomenon is shown by observing the support side of a thin nascent polyethylene film grown on glass-supported VCl_3 and having essentially a polyplike texture at its upper surface; after polymerization and subsequent washing with methanol, one finds the exact casting of the catalyst crystals with dimensions comparable with those of the polyps, as illustrated in Figure 2. This proves not only the one-to-one relation between catalyst crystal and polyp but also that in this case the catalyst has not moved from the substrate surface where it stayed firmly anchored throughout the polymerization. In the majority of cases, however, observations on the substrate side of the nascent polymer do not show any trace of the catalyst crystals although polyps, or polymer encapsulated catalyst fragments, are found throughout the thickness of the polymer films. In this case the polyethylene skin hampers contact between the inorganic nucleus of the polyp and external chemical agents. Even after thorough washing and exposure to ambient atmosphere, electron diffraction patterns of catalyst crystal can still be recorded and the purplish color of VCl_3 is apparent. Significantly, after several days this tint becomes greenish, a color associated with hydrolyzed VCl_3.

If polyps were the only morphological features of the nascent polymer films, polymerization would not go very far since the active sites would be rapidly encapsulated and as a consequence deactivated toward further polymerization. This is in fact the case for films such as the one shown in Figure 2 which remained relatively thin even after prolonged time of polymerization. Fortunately, the movement of growing polymer at the active sites on the surface of the catalyst

---

(1) H. Chanzy, A. Day, and R. H. Marchessault, *Polymer*, **8**, 567 (1967).

(2) L. A. M. Rodriguez and H. V. Van Looy, *J. Polym. Sci., Part A-1*, 4, 1971 (1966).

(3) J. Y. Guttman and J. E. Guillet, Preprints, I.U.P.A.C. Symposium of Macromolecular Chemistry, Toronto, 1968, A-6, p 24.

(4) P. Blais and R. St. John Manley, *J. Polym. Sci., Part A-1*, **6**, 291 (1968).

(5) P. Ingram and A. Schindler, *Makromol. Chem.*, **111**, 267 (1967).