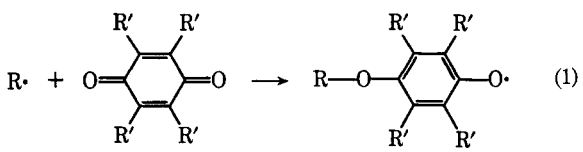
Quinone Copolymerization. III. Reactions of 2,5,7,10-Tetrachlorodiphenoquinone, *o*-Chloranil, and 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone with Vinyl Monomers under Free-Radical Initiation

C. F. Hauser*[1] and Nathan L. Zutty

Union Carbide Corporation, Chemicals and Plastics, South Charleston, West Virginia 25303. *Received February 13, 1971*

ABSTRACT: The free-radical copolymerizations of 2,5,7,10-tetrachlorodiphenoquinone, *o*-chloranil, and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone with vinyl monomers were studied. Reaction of the diphenoquinone with styrene yielded a high-molecular-weight aromatic–aliphatic polyether possessing a T_g of 150° and containing a 2:1 molar relationship of styrene:quinone. Ethyl acrylate, *N*-vinylcarbazole, and methyl α-chloroacrylate polymerized in the presence of *o*-chloranil to give polymers possessing little incorporated quinone. Styrene and 2-chlorostyrene copolymerized with *o*-chloranil to give low-molecular-weight products containing some quinone. *p*-Methoxystyrene and vinyl isobutyl ether polymerized in the presence of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone to yield homopolymers, whereas styrene, vinylidene chloride, 1,1-diphenylethylene, and tetramethylethylene copolymerized with the quinone to yield low-molecular-weight copolymers possessing aromatic–aliphatic ether linkages.

Quinones have long been associated with polymer chemistry as retarders or inhibitors to free-radical vinyl polymerization. Consensus has been that quinones retard by addition to radicals, forming relatively stable semiquinones (I) which do not add to vinyl monomer (eq 1). Some recent publications have demonstrated, however, that semiquinones (I) may add to certain vinyl monomers and to a very limited extent regenerate polymer chains.[2] Although the quinone/monomer ratios in the regenerated chains were minute, the



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I

quinones were incorporated within the chains and not present solely as end groups. More recent studies by Tudos[3] have sought to explain the quinone regenerative capacity by invokation of the hypothesis of "hot radicals" in solution.

The above facts and hypothesis imply that under the proper conditions a consistently greater degree of copolymerization could be achieved between quinone and vinyl monomer with the ultimate goal of direct formation of aromatic–aliphatic polyethers, $[-O-C_xH_y-O-CH_2-CHZ-]_n$. Previously, we reported the polymerization reactions of quinones of intermediate[4] and low[5] redox potentials with vinyl monomers. We are now reporting the reactions of quinones of high redox potentials.

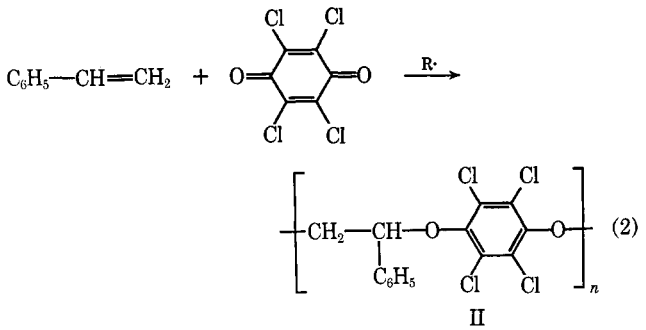
Experimental Section

Materials. The quinones were purchased and purified by threefold recrystallization from dry chloroform, benzene, or *o*-dichlorobenzene followed by two vacuum sublimation. The vinyl monomers were purified by procedures outlined in a previous paper.[5]

Polymerization Procedures. The polymerization procedures and product purification were generally similar to those used in a previous publication.[5] Part of the reaction product from styrene and 2,5,7,10-tetrachlorodiphenoquinone was generally insoluble in organic solvents. It was purified by repeated grinding with benzene in a Waring Blendor, followed by drying *in vacuo* at 40° for 24 hr.

Results and Discussion

Some years ago, Breitenbach[6] reported that styrene reacted in bulk with *p*-chloranil under free-radical conditions to yield a copolymer of 21,000 number-average molecular weight. Breitenbach's evidence (infrared data and copolymer degradation) indicated a copolymerization through the quinone carbonyl groups to give an aromatic–aliphatic polyether (II of eq 2).



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A priori, one might expect the ability of quinones to copolymerize with vinyl monomers *via* their carbonyl groups would be a function of their redox potentials (*i.e.*, a correlation between their copolymerizability and their desire to undergo reduction to the corresponding hydroquinones). A consideration would be that quinones of higher redox potentials would be more susceptible to copolymerization reactions. The first two reports in this series[4,5] dealt with quinones of low to moderate redox potentials (E_0 = 0.40–1.28). However, in neither of these reports were any apparent correlations found between the redox potentials and the

(1) To whom inquiries should be addressed.

(2) (a) J. C. Bevington, *et al.*, *Trans. Faraday Soc.*, **51**, 946 (1955); (b) *J. Chem. Soc.*, **37**, 2822 (1955); (c) J. C. Bevington and H. W. Melville, *Usp. Khim.*, **25**, 1336 (1956); (d) F. L. Funt and F. D. Williams, *J. Polym. Sci.*, **46**, 139 (1960); (e) *ibid.*, **57**, 711 (1962).

(3) F. Tudos, *Acta Chim. (Budapest)*, **44**, 403 (1965).

(4) C. F. Hauser and N. L. Zutty, *J. Polym. Sci., Part A-1*, **8**, 1385 (1970).

(5) C. F. Hauser and N. L. Zutty, *Macromolecules*, **4**, 319 (1971).

(6) J. W. Breitenbach, *Can. J. Res., Sect. B*, **38**, 507 (1950).

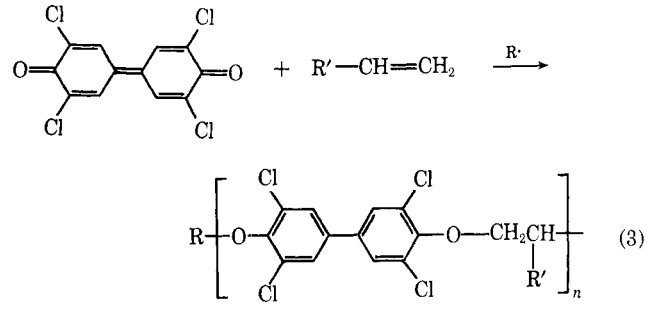
TABLE I
REACTIONS[a] OF 2,5,7,10-TETRACHLORODIPHENOQUINONE[b] (E_0 = 1.78) WITH VINYL MONOMERS

Expt no.	Monomer	Time, hr	Polymeric product	Yield, %	Reduced viscosity (solvent)	Analysis, % Carbon	Chlorine
1	Styrene	42	Yes	60[c]	1.0 (benzene)	89.53	2.29
				39[d]		62.47	24.91
2	Acrylonitrile	42	No				
3	Methyl α-chloroacrylate	42	No				
4	Vinyl acetate	42	No				
5	Tetramethylethylene	20	*e*				

[a] Reactions conducted at 70° with a 5:1 molar ratio of monomer to quinone. Benzoyl peroxide was utilized as initiator in 1.3 mol % concentration based on quinone. [b] The quinone was purified by recrystallizing three times from dry reagent grade *o*-dichlorobenzene. [c] Yield of soluble fraction based upon homopolymer of styrene. [d] Yield of insoluble fraction based upon a 2:1 copolymer of styrene–quinone. [e] Product may have been an adduct or very low-molecular-weight polymer. The contents of the reaction tube was a creamy white solid, all of which was readily soluble in methanol.

copolymerizabilities of the respective quinones. This report deals with quinones of moderate to high redox potentials (E_0 = 1.3–1.78).

Reactions of 2,5,7,10-Tetrachlorodiphenoquinone (E_0 = 1.78) with Vinyl Monomers. Bulk reactions were carried out between tetrachlorodiphenoquinone and five vinyl monomers at 70°. This type of quinone differs from the other quinones utilized in the current study in that polymerization through the carbonyl groups would afford a polyether possessing a biphenyl ring. The formation of two aromatic rings, instead of the one characteristic of *p*-benzoquinone derivatives, might provide an additional driving force for copolymerization reactions with vinyl monomers (*viz.*, eq 3). The results of the study with tetrachlorodiphenoquinone are listed in Table I.



If the formation of two aromatic rings provided additional driving force for copolymerization of the quinone, the data in Table I do not reveal it. Bulk reactions with acrylonitrile, methyl α-chloroacrylate, and vinyl acetate failed to produce any isolable polymeric products. Indeed, the reaction mixtures did not appear to undergo any change in color or consistency during the 2-day reaction periods.

Styrene, however, did copolymerize with 2,5,7,10-tetrachlorodiphenoquinone (experiment 1) to give a good yield of a polymer which was composed of soluble and insoluble fractions. The soluble fraction was obtained in 60% yield (based on styrene) and possessed a reduced viscosity of 1.0. Elemental analysis for carbon and chlorine showed this material to be composed largely of polystyrene with less than 5 wt % of incorporated quinone. An infrared spectrum and a stiffness–temperature relationship were consistent with those of commercial polystyrene.

A 39% yield of an insoluble material was also obtained from experiment 1. This polymer, which was insoluble in *N*,*N*-dimethylformamide and dimethyl sulfoxide, was composed of approximately a 2:1 molar ratio of styrene:quinone as shown by elemental analysis in carbon and chlorine. A broad, moderately intense infrared absorption was observed between 9.5 and 10.6 μ. This absorption, notably absent in the infrared spectrum of either reactant of soluble polymer fraction, looked similar to the absorption exhibited in the same region by a 1:1 copolymer of *p*-chloranil and styrene[4] and is indicative of a polyether linkage. To this end, it is noteworthy that the copolymer exhibited no carbonyl absorptions in the infrared.

The insolubility of the second fraction from experiment 1 implies a degree of cross-linking. However, the nature and extent of the cross-linking reaction are presently unknown.

A stiffness–temperature relationship of a molded plaque of the insoluble copolymer is of interest, and the experimental plot, shown in Figure 1, is markedly different from that of commercial polystyrene (T_g 100°). A T_g was observed in the region of 150°, which implies that the material is an aromatic–aliphatic polyether of quite high molecular weight. Moreover, the shape of the stiffness–temperature plot (*i.e.*, its difference from the plot of polystyrene) demonstrated that the copolymer definitely contained incorporated tetrachlorodiphenoquinone. We postulate the copolymer structure to be similar to that shown in eq 3, except that two styrene molecules are incorporated per molecule of quinone.

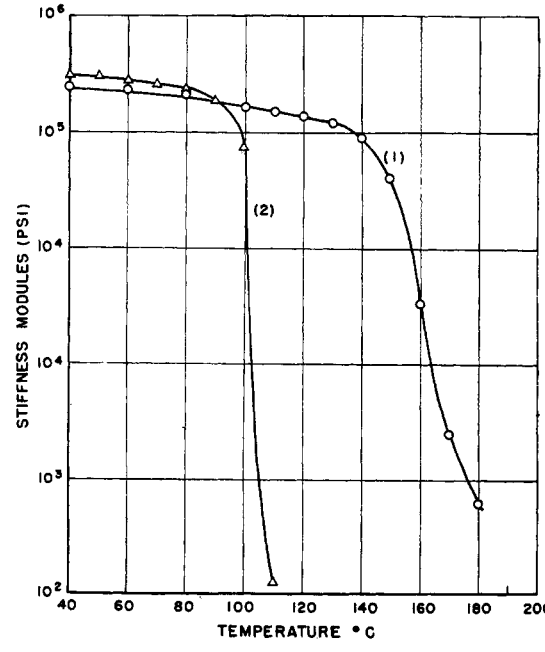


Figure 1. Stiffness–temperature relations of (1) styrene–2,5,7,10-tetrachlorodiphenoquinone copolymer and (2) commercial polystyrene.

TABLE II
REACTIONS[a] OF *o*-CHLORANIL[b] (E_0 = 1.3) WITH VINYL MONOMERS

Expt no.	Monomer	Time, hr	Polymer product	Yield, %	Reduced viscosity (solvent)	Analysis, % Carbon	Chlorine
1	Styrene	42	Yes	9[d]	0.08 (benzene)	79.34	8.08
2	Acrylonitrile	42	No				
3	Vinylidene chloride	42	No				
4	Ethyl acrylate	42	Yes	25[c]	0.43 (benzene)	59.40	1.06
5	*N*-Vinylcarbazole[e]	42	Yes	38[c]	0.35 (DMF)	86.62	0.93
6	Tetramethylethylene	16	No[f]				
7	Tetrachloroethylene	42	No				
8	Methyl α-chloroacrylate	42	Yes	51[c]	0.09 (DMSO)	39.41	29.83
9	Vinyl isobutyl ether	42	No				
10	2-Chloroacrylonitrile	42	No				
11	Vinyl acetate	42	No				
12	2-Chlorostyrene	42	Yes	58[d]	0.17 (benzene)	65.31	22.31

[a] Reactions conducted at 70° with a 4:1 molar ratio of monomer:quinone. Benzoyl peroxide utilized as initiator in 1.3 mol % based on quinone. [b] *o*-Chloranil recrystallized three times from dry benzene and sublimed twice. [c] Yield based upon homopolymer. [d] Yield based upon copolymer of 10:1 molar incorporation of styrene:quinone. [e] Quinone and monomer used in 1:1 molar ratio in chlorobenzene solvent. [f] Product was soluble in methanol and was not isolated.

The final reaction in Table I, the bulk reaction with tetramethylethylene, afforded a good yield of a creamy white product after less than 1 day at 70°. The material did not appear to be of significant molecular weight, since it was completely soluble in methanol. This product was either a simple adduct or a very low-molecular-weight polymer, and no effort was made to isolate it from the methanol solution.

Reactions of *o*-Chloranil (E_0 = 1.3) with Vinyl Monomers. *o*-Chloranil was allowed to react with 12 vinyl monomers at 70° and the results of these reactions are shown in Table II. Although this quinone is known to undergo a variety of molecular addition reactions with olefins, we felt that the proper combination of reaction conditions and vinyl monomers could lead to copolymer products. Polyethers of unusual conformation could arise by copolymerization through the ortho keto groups of the quinone.

o-Chloranil, however, did not show any general reactivity toward the vinyl monomers listed in Table II. Bulk reactions with acrylonitrile, vinylidene chloride, tetrachloroethylene, vinyl isobutyl ether, 2-chloroacrylonitrile, and vinyl acetate did not provide any polymeric products. Following initial mixing, none of these reactions mixtures appeared to change in color or consistency during the 2-day reaction periods.

The bulk reaction with styrene, however, produced a polymeric product in low yield of reduced viscosity 0.08 (experiment 1). Elemental analyses for carbon and chlorine showed that 20 wt % *o*-chloranil had been incorporated into the copolymer. An infrared spectrum exhibited a very weak absorbance at 5.8 μ and a modest absorbance at 9.7 μ. This latter absorbance had similar position and appearance to the absorbance normally associated with the ether linkage of the *p*-chloranil–styrene copolymer,[4] and probably arose from an aliphatic–aromatic ether linkage. Whatever the structure of this copolymer, however, *o*-chloranil did not copolymerize with styrene as readily as did the para isomer. Under similar conditions, *p*-chloranil reacted with styrene to provide a 48% yield of an alternating 1:1 copolymer of reduced viscosity 0.10.[4]

Bulk reactions with ethyl acrylate and methyl α-chloroacrylate (experiments 4 and 8, respectively) and the chlorobenzene solution reaction with *N*-vinylcarbazole (experiment 5) afforded moderate yields of polymeric products of reduced viscosities 0.43, 0.09, and 0.35, respectively. However, elemental analysis for carbon and chlorine showed these materials to be essentially homopolymers of the respective vinyl monomers with little incorporated quinone. An infrared spectrum of each polymer agreed well with that expected for the homopolymer.

Tetramethylethylene reacted in bulk with *o*-chloranil (experiment 6), but apparently did not give a polymeric product of significant molecular weight. After less than 2 days at 70°, the reaction mixture was composed of a clear, brown supernatant liquid and a gray solid. The solid, which was not purified, was soluble in methanol and may have been a charge-transfer complex between the donor ethylene and the quinone.

The bulk reaction with 2-chlorostyrene, the last experiment in Table II, afforded a good yield of a polymeric product of reduced viscosity 0.17 in benzene. Elemental analysis for carbon and chlorine indicated that the polymer was composed largely of poly(2-chlorostyrene) with less than 5 wt % incorporated quinone. An infrared spectrum of the reaction product agreed moderately well with a spectrum of poly(2-chlorostyrene).

Reactions of 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (E_0 = 1.78). 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) was allowed to react with 20 vinyl monomers at 70° with benzoyl peroxide initiator, and the results of these experiments are recorded in Table III. DDQ was generally more soluble in the various vinyl monomers than the other quinones utilized in this study, and it was expected that its good solubility and high redox potential would facilitate its copolymerization with vinyl monomers. However, this expectation did not materialize. The few polymerization reactions which did occur did not yield high-molecular-weight products.

The bulk reactions of DDQ with acrylonitrile, ethyl acrylate, vinyl acetate, maleic anhydride, bicycloheptene, methyl α-chloroacrylate, 2-chloroacrylonitrile, trichloroethylene, tetrachloroethylene, and trimethylethylene and the chlorobenzene solution reactions of vinyltriphenylsilane, *N*-vinylcarbazole, and 1,1- and 1,2-bis(*p*-methoxyphenyl)ethylene failed to yield any isolable products. No change in color or consistency was observed in any of the reaction tubes over the course of the 2-day reaction periods.

Styrene (experiment 1) did undergo a bulk reaction with DDQ to afford an excellent yield (88%) of a material of reduced viscosity 0.04. Elemental analyses for carbon and chlorine indicated a 1:1 copolymer, albeit of low molecular

TABLE III
REACTIONS[a] OF 2,3-DICHLORO-5,6-DICYANO-*p*-BENZOQUINONE[b] (E_0 = 1.78) WITH VINYL MONOMERS

Expt no.	Monomer	Time, hr	Solvent[c]	Polymeric product	Yield, %	Reduced viscosity (solvent)	Analysis, % Carbon	Chlorine
1	Styrene	40	Monomer	Yes	88[d]	0.04 (benzene)	59.89	19.49
2	Acrylonitrile	40	Monomer	No				
3	Vinylidene chloride	40	Monomer	Yes	22[d]	0.05 (DMF)	39.10	42.75
4	Ethyl acrylate	40	Monomer	No				
5	Vinyl acetate	40	Monomer	No				
6	*p*-Methoxystyrene	40	Monomer	Yes	23[e]	0.08 (DMF)	77.44	2.30
7	Maleic anhydride	40	Monomer	No				
8	Bicycloheptene	40	Monomer	No				
9	*N*-Vinylcarbazole	40	Chlorobenzene	No				
10	1,1-Bis(*p*-methoxyphenyl)ethylene	40	Monomer	No				
11	1,2-Bis(*p*-methoxyphenyl)ethylene	40	Monomer	No				
12	1,1-Diphenylethylene	40	Monomer	Yes	6[d]	0.08 (benzene)	72.55	12.65
13	Methyl α-chloroacrylate	40	Monomer	No				
14	2-Chloroacrylonitrile	40	Monomer	No				
15	Vinyl isobutyl ether	40	Monomer	Yes	23[e]	0.10 (benzene)	68.18	4.70
16	Vinyltriphenylsilane	42	Chlorobenzene	No				
17	Trichloroethylene	42	Monomer	No				
18	Tetrachloroethylene	42	Monomer	No				
19	Trimethylethylene	42	Monomer	No				
20	Tetramethylethylene	42	Monomer	Yes	58[d]	0.02 (DMF)	54.83	22.00

[a] Reactions conducted at 70° with 1.3 mol % benzoyl peroxide initiator; catalyst concentration based upon quinone. [b] Quinone purified by recrystallization three times from dry chloroform in an inert atmosphere. [c] When monomer is referred to as solvent, 4 equiv of monomer/equiv of quinone is employed; when a special solvent is used, the quinone and monomer are in a 1:1 molar ratio. [d] Yield based upon quinone and a 1:1 copolymer. [e] Yield based upon homopolymer of vinyl monomer.

weight. An infrared spectrum of the material was void of carbonyl and phenoxy absorptions, peaks for which are usually observed with low-molecular-weight quinone reaction products.[4] A weak absorbance was observed at 4.4 μ indicating the presence of undisturbed nitrile moieties. A strong, broad absorbance was noticed in the vicinity of 9.4–10.1 μ and could have arisen from an aliphatic–aromatic ether linkage; the absorption was similar to that observed with *p*-chloranil–styrene copolymers.[4] Based on this evidence, it would appear that the DDQ copolymerized *via* its carbonyls to yield a low-molecular-weight polyether.

Vinylidene chlorine (experiment 3) underwent a bulk reaction with DDQ to afford a 22% yield of a material of reduced viscosity 0.05. Elemental analyses for carbon and chlorine showed the reaction product to be a 1:1 copolymer. As in the case of the styrene–DDQ copolymer, no infrared absorptions characteristic of carbonyl or phenoxy were observed. A weak nitrile band was noted at 4.4 μ and a series of three broad bands was observed between 9.0 and 10.1 μ. These latter absorbances could have arisen from an ether linkage, although they did not possess the same shapes as the absorbances assigned to quinone-derived polyethers.[4,6]

Both *p*-methoxystyrene (experiment 6) and vinyl isobutyl ether (experiment 15) polymerized in the presence of DDQ to yield polymeric products possessing small amounts of incorporated quinone. The *p*-methoxystyrene product exhibited a reduced viscosity of 0.08 and was shown by elemental analysis for carbon and chlorine to contain less than 5 wt % incorporated DDQ. The vinyl isobutyl ether product possessed less than 10 wt % incorporated DDQ and a reduced viscosity of 0.10. The infrared spectra of both products were reasonably consistent with those expected for the homopolymer.

1,1-Diphenylethylene (experiment 12) reacted in bulk with DDQ to produce a 6% yield of a polymeric product possessing a reduced viscosity of 0.08. Elemental analyses for carbon and chlorine showed a 2:1 molar relationship of ethylene:quinone. An infrared spectrum showed a weak absorption of 6.1 μ and a strong absorption, probably arising from an aliphatic–aromatic ether linkage, at 9.2–9.4 μ. No phenoxy absorbances were noted. The quinone appears to have copolymerized predominately *via* its carbonyls to yield a polyether.

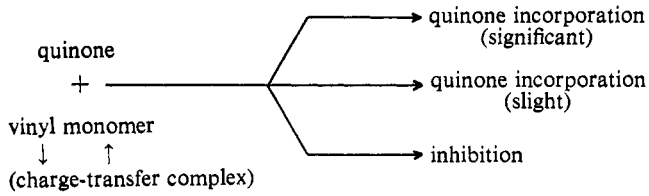
The last experiment in Table III, the bulk reaction of tetramethylethylene, afforded a good yield of material of reduced viscosity 0.02 in DMF. The reaction mixture set up to a white solid in less than 2 days at 70°. Elemental analysis for carbon and chlorine showed the material to be a copolymer of a 1:1 molar relationship between ethylene and quinone. An infrared spectrum possessed a very strong absorbance at 5.8 μ, but only a very slight one at 4.4 μ. The lack of appreciable absorbance at the latter wavelength would indicate that the nitrile groups of the DDQ were somehow involved in the reaction with the vinyl monomer. No absorbance bands were observed in the infrared region normally characteristic of ether linkages (9.0–10.0 μ). Although the structure of the material is unknown, predominant reaction did not appear to be *via* the quinone carbonyls to yield polyether.

The inability of the vinyl monomers to form copolymers of appreciable molecular weights with the high redox DDQ is interesting. Indeed, none of the observed products possessed reduced viscosities in excess of 0.1. With the exception of tetramethylethylene, however, none of the obtained products possessed infrared carbonyl absorbances, implying that the carbonyls were involved in the copolymerizations to afford polyethers, albeit at low molecular weights.

Conclusion

A general classification of the reaction of 2,5,7,10-tetrachlorodiphenoquinone, *o*-chloranil, and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone with vinyl monomers is shown in Scheme I. With 2,5,7,10-tetrachlorodiphenoquinone, "significant" quinone incorporation was observed with styrene,

SCHEME I



but inhibition with the other monomers. Two examples of significant incorporation and three examples of "slight" incorporation were observed with *o*-chloranil, whereas 2,3-dichloro-5,6-dicyano-*p*-benzoquinone afforded four significant incorporations and two slight. In general, however, only inhibition was observed in reactions with these quinones. We do not know to what extent charge-transfer complexes influenced the observed polymerization reactions and, conversely, the inhibition to reaction. The facts that coloration almost always occurred upon admixture of quinone and vinyl monomer and that quinones are known electron acceptors attest to the presence of CT complexes in the reaction mixtures, if not to their direct participation.

We conclude that although some quinones can copolymerize with some vinyl monomers under free-radical conditions, the quinone copolymerizability and its redox potential are not generally related. Quinones of low, moderate, and high redox potentials have been treated with vinyl monomers over a wide range of double bond activity,[4,5] but the observed copolymerization reactions were spotty and inconsistent. However, some interesting copolymers were obtained from the present study, some of which arose by copolymerization *via* the quinone carbonyl groups to yield aliphatic–aromatic polyethers. The most significant example of an aromatic–aliphatic polyether obtained from the work presented in this paper was the product from 2,5,7,10-tetrachlorodiphenoquinone and styrene, wherein a high-molecular-weight copolymer was realized. We feel that other polyethers of high molecular weights can be prepared by use of quinones as comonomers, provided the proper reaction conditions are found.

Ethylene–Propylene Copolymers. Reactivity Ratios, Evaluation, and Significance

C. Cozewith* and G. Ver Strate

Enjay Polymer Laboratories, Linden, New Jersey 07036. *Received January 15, 1971*

ABSTRACT: Reactivity ratios have been determined in ethylene–propylene copolymerization for a number of Ziegler–Natta catalyst systems. It was found that the reactivity ratio products varied with the composition of the catalyst components and were generally less than 0.5. A critical survey was also made of other published values for ethylene–propylene reactivity ratios. Considerable disagreement exists, which was primarily attributed to the method of copolymer analysis and the presence of multiple active species which are formed by many soluble Ziegler–Natta catalysts. It is shown that if multiple species are present, the reactivity ratios are a function of the mode of catalyst addition. Also, the reactivity ratios determined from the normal copolymerization equation do not correctly predict the sequence distribution in the copolymer.

The composition of the Ziegler catalyst used to produce ethylene–propylene rubber has a profound effect on both the polymerization process and the polymer properties. This effect arises in part from the variation in copolymerization reactivity ratios that occurs with a variation in catalyst system components. The value of the reactivity ratios (under otherwise constant copolymerization conditions) determines not only the relative monomer conversions but also the distribution of monomer sequences in the polymer chain. This distribution is of particular importance in ethylene–propylene rubber since the polymer crystallinity that results from long ethylene sequences affects the mechanical performance of the finished goods and the rheological behavior during processing.

Reactivity ratios for ethylene–propylene copolymerization with soluble Ziegler catalysts have been reported in the literature (see Table III), and some attempts have been made to relate these parameters to the monomer sequence distribution in the copolymer chain.[1–4] There is also information available on how the values of the reactivity ratios actually affect polymer crystallinity. This work was carried out to investigate that relationship further, and also to elucidate the dependence of the reactivity ratios on the components of the Ziegler catalyst.

We feel that this study makes at least two useful contributions. First, extensive efforts are made to use correct experimental and numerical techniques in the collection and evaluation of data. Second, the significance of the reactivity ratios and the reactivity ratio product as defined in the terminal copolymerization model[5] is explored with regard to its correlation with the actual properties of the polymers obtained when they are produced by catalysts which commonly have multiple active polymerization centers.

Experimental Section

(A) Materials. The polymerization solvents, *n*-heptane (Phillips, 99 mol % minimum) and chlorobenzene (Matheson Coleman and Bell, bp 130–132°), were dried by passage through a column of 4A molecular sieves and were then stored under nitrogen until used. The *n*-heptane also obtained additional purification by treatment with silica gel.

Oxygen and water were removed from the ethylene and propylene (99 mol %, purchased from J. T. Baker) by passage at 100 psig

(1) C. Tosi, A. Valvassori, and F. Ciampelli, *Eur. Polym. J.*, **5**, 575 (1969).
(2) Th. A. Veerkamp and A. Veermans, *Makromol. Chem.*, **58**, 147 (1961).
(3) J. P. Jackson, *J. Polym. Sci., Part A*, **1**, 2119 (1962).
(4) G. Ver Strate, and Z. W. Wilchinsky, *ibid., Part A-2*, **9**, 127 (1971).
(5) G. E. Ham, "Copolymerization," Interscience, New York, N. Y., 1964, p 3.