Examination of the data and Figures 2 and 3 shows that, with vinyl acetate, the terminal complex model gives a better fit than that with the parameters chosen by Hecht.[6] However, he set r' $(=k_{221}/k_{212}) = 0$. A judicious choice of r' could give a better fit. As can be seen, one cannot choose easily between the models in the styrene case, within the possible experimental errors. Here, one cannot even choose between the possibilities of whether a radical attacks the A or B side of a complex. This is due to the high reactivity ratios. However, polymerization in a solvent should fix r_{12} and decide the question. Probably, the B side is attacked as this produces a stable styryl radical at the polymer end.

Another difficult point is interpretation of the data at high TCCP ratios. This is suspect, as the molecular weights are quite low (about 2000). Thus, end effects could lower or raise the mole ratios depending on the assumed termination steps. This can be seen, for example, in the complex I curve in Figure 2. Here the curve is within ±0.01 mol fraction of the experimental points, except for the last point.

Finally, we can compare the reactivity ratios in Table IV. One might expect that r_{12} for vinyl acetate should be closer to 12 than to 33 since r_{12} for styrene is about 19. The lack of sensitivity indicates that most of the incorporation of TCCP with vinyl acetate occurs through the complex. On the other hand, r_{1C}/K for styrene is about 65 compared to about 8.5 for vinyl acetate. Therefore, complex copolymerization of TCCP with styrene is relatively unimportant except at high mole fractions of A.

It is possible too that in this case a true steric penultimate effect or reversible copolymerization may be occurring.[7] This could be settled by copolymerization at lower temperatures. Since in the VAc–TCCP copolymer, an m_2 of 0.35 was found, lowering the polymerization temperature should raise this rapidly toward 0.5. If complexes are operating, the change should be slight and related to changes in the equilibrium constant with temperature.

In summary, copolymerization of vinyl acetate with fluorochloroacetones and vinyl acetate and styrene with TCCP both can be rationalized by a terminal complex copolymerization model as well as or better than by a penultimate model. It is truly remarkable how well two different equations can fit the same data. As usual, changing from a less to a more reactive comonomer (4FK to 6FK with vinyl acetate, styrene to vinyl acetate with TCCP) lowers the reactivity ratios and the copolymer curves show greater alternation. Neither paper gives sufficient data to allow a choice between models. One needs solution polymerization at various dilutions to decide.

Quinone Copolymerization. II. Reactions of 1,4,5,8-Tetrachloroanthraquinone, 2,3-Dichloro-1,4-naphthoquinone, and 2,3,5,6-Tetramethyl-*p*-benzoquinone with Vinyl Monomers under Free Radical Initiation

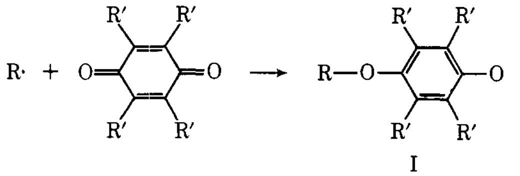
C. F. Hauser[1] and Nathan L. Zutty

Union Carbide Corporation, Chemicals and Plastics, South Charleston,
West Virginia 25303.

Received December 18, 1970

ABSTRACT: The copolymerization reactions of certain vinyl monomers with 1,4,5,8-tetrachloroanthraquinone, 2,3-dichloro-1,4-naphthoquinone, and 2,3,5,6-tetramethyl-*p*-benzoquinone were studied. No general correlations were observed between the quinone redox potentials and their copolymerizability with vinyl monomers. The 1,4,5,8-anthraquinone copolymerized readily with a variety of monomers to afford high molecular weight products. The mechanism proposed for these reactions involves a 1,4-butadiene-type addition of the vinyl monomer to the fused ring(s) of the anthraquinone. In contrast to the anthraquinone reactions, neither the naphthoquinone nor the tetramethylbenzoquinone showed a general tendency to copolymerize with the vinyl monomers. However, interesting polymeric products were obtained from some of the reaction mixtures of these latter quinones.

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 on the inhibition of vinyl polymerization by quinones, however, have demonstrated that semiquinones (I) once formed do not always assume a passive role. Indeed, some of these species were active enough to 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 quinones were incorporated within the chains and not present solely as end groups.



I

(1)

More recently, Tudos[3] studied the inhibition to vinyl polymerization by certain quinones and observed the occasional incorporation of quinone into the polymer products. As an explanation for the incorporation phenomenon, Tudos

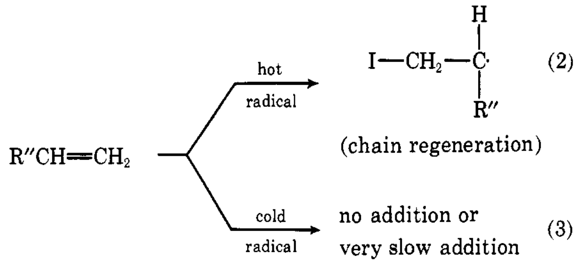
---

(1) To whom inquiries should be addressed.

(2) (a) J. C. Bevington, *et al.*, *Trans. Faraday Soc.*, **51**, 946 (1955); (b) *J. Chem. Soc.*, 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. Acad. Sci. Hung.*, **44**, 403 (1965).

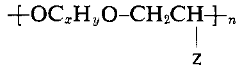
invoked the hypothesis of "hot radicals" in solution. In this hypothesis a vibrationally hot semiquinone (I), generated *via* reaction of quinone with radical, may either use its excess energy for reaction with vinyl monomer and regeneration of the polymer chain (eq 2), or transfer that energy of the medium and yield an inactive (cold) radical (eq 3).



(2)

(3)

The above facts and hypothesis imply that under the proper conditions a considerably greater degree of copolymerization could be achieved between quinone and vinyl monomer with the ultimate goal of direct formation of aromatic–aliphatic polyethers.



$$-\!\!\left[OC_xH_yO\text{-}CH_2\underset{\displaystyle Z}{CH}\right]\!\!-_n$$

Previously, we reported the polymerization reactions of quinones of intermediate redox potentials with vinyl monomers.[4] We are now reporting the reactions of quinones of low redox potentials.

Experimental Section

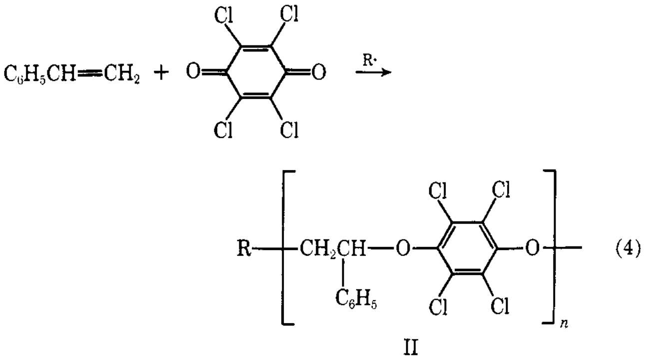
Materials. The quinones were purchased and the 2,3-dichloro-1,4-naphthoquinone and the 1,4,5,8-tetrachloroanthraquinone were purified by recrystallization three times from benzene and *o*-dichlorobenzene, respectively. Duroquinone was recrystallized three times from ethanol–water, followed by two vacuum sublimations. The vinyl monomers were purified by distillation through a spinning band distillation column or by repeated recrystallization from dry solvents. The solvents were dried over 4-A molecular sieves (product of Union Carbide Corp.) and distilled through a spinning band column.

Polymerization Procedures. While under a nitrogen atmosphere, pressure tubes were charged with reactants, solvent (if other than vinyl monomer), and catalyst. The tubes were capped and placed in a rotating constant-temperature bath. Upon completion of the desired reaction periods, the contents of each tube were mixed with enough benzene (dimethyl sulfoxide or *N,N*-dimethylformamide if the polymer was insoluble in benzene) to give a pourable solution, and insoluble quinone removed by filtration. The filtrate was poured with stirring into a large excess of methanol, and the precipitated product, if any, collected by filtration. Final purification was accomplished by solution–precipitation (three times) from benzene (or DMF)–methanol, whereupon the product was dried *in vacuo* at 40° for 24 hr. If the polymer product was insoluble in organic solvents, it was purified by repeated grinding with methanol in a Waring Blendor, whereupon it was dried *in vacuo* at 40° for 24 hr.

The stiffness–temperature relationship of the 1,4,5,8-tetrachloroanthraquinone–styrene copolymer was determined by experiment on an Instron tester. Reduced viscosities were measured in a Ubbelohde viscometer at 25° and a concentration of 0.2 g/d.

Results and Discussion

Some years ago, Breitenbach[5] 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 4).



(4)

II

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). The first report in this series[4] dealt with quinones of intermediate redox potentials (E_0 = 0.60–1.28). However, no general correlations were found between the redox potentials and the copolymerizabilities of those quinones. This report deals with quinones of low redox potentials (E_0 = 0.40–0.50).

Reactions of 1,4,5,8-Tetrachloroanthraquinone ($E_0 \sim$ 0.4) with Vinyl Monomers. Perhaps the most interesting and certainly the most productive set of experiments of the current study was the reactions with 1,4,5,8-tetrachloroanthraquinone. This remarkable quinone copolymerized with five of the six tested vinyl monomers. The results of these reactions are recorded in Table I, wherein a 4:1 molar excess of vinyl monomer–quinone was employed in each reaction.

The reaction with styrene at 70° (expt no. 1) yielded a solid reaction mass in less than 2 days. A copolymer of reduced viscosity 0.32 (DMF) was isolated in good yield, which was shown by elemental analysis for carbon and chlorine to contain 27 wt % of incorporated quinone (10.0 mol %). This copolymer exhibited a weak infrared carbonyl absorption of 5.9 μ and other weak absorptions characteristic of the tetrachloroanthraquinone. A stiffness–temperature relationship of the copolymer showed a marked difference from that of commercial polystyrene (see Figure 1). A single transition near 100° is seen with polystyrene, whereas two distinct transitions, one at 60° and one at 90°, were observed with the copolymer.

The reaction of acrylonitrile with 1,4,5,8-tetrachloroanthraquinone, expt 2 of Table I, afforded a good yield of copolymer of reduced viscosity 3.0 (DMF). An infrared spectrum of the copolymer exhibited a moderate strength carbonyl absorption at 5.9 μ, and elemental analysis for carbon and chlorine indicated 48 wt % of incorporated quinone (12.5 mol %).

Reaction of 1,4,5,8-tetrachloroanthraquinone with vinyl acetate (expt no. 3) failed to produce any polymeric product. No change in color or consistency was observed in the reaction mixture during the 2-day reaction period.

Methyl α-chloroacrylate (expt no. 4) was found to copolymerize in bulk with the quinone to provide an excellent yield of copolymer of reduced viscosity 1.35 (DMSO). Analyses for carbon and chlorine indicated that 32 wt % of quinone had been incorporated into the copolymer (14.3 mol %). Infrared absorbances characteristic of both the monomer quinone and polyacrylate were observed.

Ethyl acrylate and vinylidene chloride were found to

---

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

[5] J. W. Breitenbach, *Can. J. Res.*, **28B**, 507 (1950).

TABLE I

REACTIONS[a] OF 1,4,5,8-TETRACHLOROANTHRAQUINONE[b] WITH VINYL MONOMERS

Expt no.	Monomer	Time, hr	Yield,[c] %	Reduced viscosity (solvent)	Analysis, % C	Analysis, % Cl	Ratio[e]
1	Styrene	42	69.5	0.32 (DMF)	81.07	11.07	9:1
2	Acrylonitrile	42	74.0	3.0 (DMF)	58.38	19.56	7:1
3	Vinyl acetate	42					
4	Methyl α-chloroacrylate	42	56.7	1.35 (DMSO)	42.65	32.84	6:1
5	Ethyl acrylate	20	76.4	*d*	56.45	12.01	8:1
6	Vinylidene chloride	20	90.6	*d*	31.68	62.21	7:1

[a] Reactions conducted at 70° with 1.3 mol % benzoyl peroxide initiator (based on quinone). Utilized 4 equiv of vinyl monomer per equivalent of quinone. [b] Obtained from Du Pont and recrystallized three times from dry *o*-dichlorobenzene. [c] Yields based upon moles of quinone charged and ratio of incorporated vinyl monomer to quinone. [d] Copolymer too insoluble in organic solvents to allow reduced viscosity measurement at 0.2 g/dl. [e] Molar ratio of vinyl monomer–quinone incorporated into copolymer.

undergo reactions with the anthraquinone to provide solid reaction masses in less than 2 days (expt no. 5 and 6, respectively). Each of the resulting copolymers was generally insoluble in organic solvents, however, and could be purified only by repeated grinding with methanol in a Waring Blendor. Although the grindings were continued until the color of monomer quinone could no longer be detected in the methanol washings, this technique may not have completely removed all of the quinone. Nevertheless, elemental analyses of carbon and chlorine indicate a 30 wt % incorporation of quinone into the ethyl acrylate copolymer (11.1 mol %) and a 33.7 wt % incorporation into the vinylidene chloride copolymer (12.5 mol %). An infrared spectrum of the vinylidene chloride copolymer exhibited absorption bands characteristic of both the monomer quinone and poly(vinylidene chloride). The ethyl acrylate copolymer was a rubber-like material which could not be ground into a pellet with potassium bromide, and its infrared spectrum was not taken.

The observation that 1,4,5,8-tetrachloroanthraquinone would copolymerize with styrene, acrylonitrile, methyl α-chloroacrylate, ethyl acrylate, and vinylidene chloride is quite interesting. Although the other quinones utilized in this study[4] copolymerized with some of these vinyl monomers, none possessed the general tendency toward formation of high molecular weight copolymers which was characteristic of the tetrachloroanthraquinone. The inability of this quinone to copolymerize with vinyl acetate may be representative of an upper energy limit of the corresponding semiquinone radical. If it is conceded that chain propagation was by a free radical mechanism, the semiquinone radical might have possessed insufficient strength to add to vinyl acetate and generate the strong vinyl acetate radical.

The copolymers derived from acrylonitrile, methyl α-chloroacrylate, and vinylidene chloride were more brittle than commercial polystyrene. Plaques pressed from these materials were extremely brittle and disintegrated before stiffness–temperature relationships could be determined. The copolymer derived from ethyl acrylate was a tough, rubbery material and could not be pressed into a plaque.

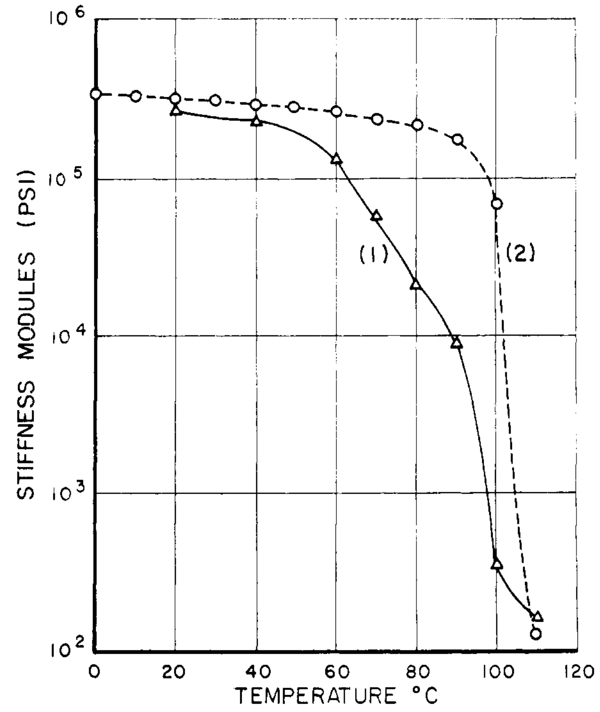
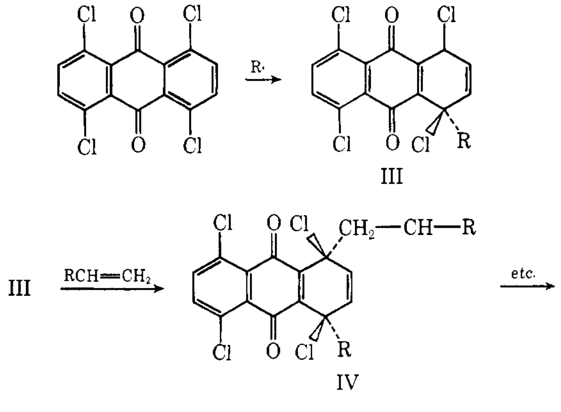


Figure 1. Stiffness-temperature relationships of (1) styrene/1,4,5,8-tetrachloroanthraquinone copolymer and (2) commercial polystyrene.

The mechanism by which 1,4,5,8-tetrachloroanthraquinone copolymerized with the vinyl monomers for the copolymerization reactions is of considerable interest. Each copolymer possessed an infrared carbonyl absorption at a wavelength similar to that of the quinone monomer and roughly in proportion to the weight per cent of incorporated quinone. If free radical chain propagation is assumed, the presence of a quinone carbonyl absorption in each copolymer would imply that the quinone was incorporated by some mechanism other than *via* its carbonyl groups (*i.e.*, reactions to form products other than aliphatic–aromatic polyethers).

We propose, therefore, that copolymerization occurred by way of the 1,4 position of the anthraquinone (eq 5). Radi-



(5)

TABLE II
REACTIONS[a] OF 2,3-DICHLORO-1,4-NAPHTHOQUINONE[b] WITH VINYL MONOMERS

Expt no.	Monomer	Time, hr	Solvent[c]	Polymeric product	Yield, %	Reduced viscosity (solvent)	Analysis, %	
							C	Cl
1	Styrene	40	Monomer	No				
2	Acrylonitrile	40	Monomer	Yes[d]	93[e]	3.77 (DMF)	65.57	1.34
3	Vinylidene chloride	42	Monomer	Yes[f]	20[e]	Insoluble		62.55
4	Ethyl acrylate	40	Monomer	No				
5	Vinyl acetate	40	Monomer	No				
6	Methyl α-chloroacrylate	40	Monomer	Yes	71[e]	1.68 (DMF)		29.40
7	2-Chloroacrylonitrile	40	Monomer	No				
8	*p*-Methoxystyrene	42	Monomer	Yes	90[e]	0.05 (benzene)	80.41	0.35
9	Vinyl isobutyl ether	42	Monomer	No				
10	2-Chlorostyrene	42	Monomer	Yes[d]	85[e]	0.13 (benzene)		25.31
11	Vinyltoluene	42	Monomer	Yes	4[g]	0.06 (benzene)		13.66
12	1,1-Bis(*p*-methoxyphenyl)-ethylene	42	Chlorobenzene	No				
13	*N*-Vinylcarbazole	42	Chlorobenzene	Yes[d]	66[e]	0.25 (benzene)	85.92	0.69

[a] Reactions conducted at 70° with 1.3 mol % benzoyl peroxide initiator (based on quinone). [b] Quinone purified by threefold recrystallization from dry benzene. [c] When monomer is referred to as solvent, a 4:1 molar ratio of monomer to quinone was employed. When a special solvent is used, the reactants are in a 1:1 molar ratio. [d] Polymer contained less than 5 wt % incorporated quinone. [e] Yield based on homopolymer. [f] Polymer contained 20 wt % incorporated quinone. [g] Yield based on 2:1 molar ratio of comonomers.

cal attack on either side of the quinone would result in 1,4-butadiene-like addition and the resulting radical III, which could continue chain propagation by reaction with vinyl monomer. Copolymerization on either or both sides, as shown in eq 5, would preserve the conjugated ketone system and not appreciably alter the position of its infrared absorption. Indeed, the insoluble products obtained from reactions with ethyl acrylate and with vinylidene chloride may have resulted from cross-linking *via* copolymerizations along both sides of the quinone.

Relief of steric crowding within the 1,4,5,8-tetrachloroanthraquinone molecule might be the driving force for the copolymerization reactions observed with this quinone. Models show relief of steric crowding between the carbonyl and the chloro groups could result as a consequence of the proposed mechanism. The probable increase in energy of product IV would necessarily be overbalanced by energy decrease associated with chlorine–oxygen crowding in the parent quinone. If the copolymerization of 1,4,5,8-tetrachloroanthraquinone did occur by the mechanism shown in eq 5, it would constitute a new type of polymerization system. To our knowledge, 1,4-butadiene-like copolymerization with anthraquinone derivatives has not been observed before and should offer a fertile field for investigation. Probably, higher quinone incorporation ratios can be achieved if solvents more suitable to solvation of the anthraquinone than the employed vinyl monomers are utilized. The anthraquinone was generally of limited solubility in all the vinyl monomers.

Reactions of 2,3-Dichloro-1,4-naphthoquinone (E_0 = 0.5) with Vinyl Monomers. Although 2,3-dichloro-1,4-naphthoquinone showed no general tendency to form copolymers when treated with vinyl monomers, the reactions of vinyl monomers in its presence are interesting and are recorded in Table II. All reactions were conducted at 70° under benzoyl peroxide initiation. A 4:1 molar ratio of reactants (comonomer–quinone, respectively) was utilized with the bulk reactions, whereas a molar ratio of 1:1 was used for reactions involving a special solvent.

Bulk reactions with styrene, ethyl acrylate, vinyl acetate, 2-chloroacrylonitrile and vinyl isobutyl ether, and the reaction of 1,1-bis(*p*-methoxyphenyl)ethylene in the presence of chlorobenzene all failed to produce isolable polymeric products. None of these reaction mixtures appeared to undergo variation in color or consistency during the 2-day reaction periods.

A bulk reaction with acrylonitrile (expt no. 2) afforded an excellent yield of polymeric material of reduced viscosity 3.77 (DMF). Analysis for carbon and chlorine indicated this polymer to consist largely of polyacrylonitrile with less than 5 wt % of incorporated quinone. In consideration of the Mark–Houwink calculations[4,6] (intrinsic viscosity–molecular weight relationship) for acrylonitrile–*p*-chloranil copolymers, the quinone was present within the polymer chain and not present solely as end groups.

The bulk reaction with vinylidene chloride (expt no. 3) produced a low yield of polymeric product which was generally insoluble in organic solvents. However, a white powder was obtained following repeated grinding with *N*,*N*-dimethylformamide in a Waring Blendor. Elemental chlorine analysis showed the polymer to contain 25 wt % incorporated quinone (approximately seven monomer units per quinone).

Methyl α-chloroacrylate (expt no. 6), *p*-methoxystyrene (expt no. 8), 2-chlorostyrene (expt no. 10), and *N*-vinylcarbazole (expt no. 13) polymerized in the presence of 2,3-dichloro-1,4-naphthoquinone to yield polymeric products of reduced viscosities 1.68 (DMF), 0.05 (benzene), 0.13 (benzene), and 0.25 (benzene), respectively. However, elemental chlorine analysis showed each material to consist largely of the homopolymer of the vinyl monomer with little incor-

---

(6) R. L. Cleland and W. H. Stockmayer, *J. Polym. Sci.*, **17**, 473 (1955).

TABLE III

REACTIONS[a] OF 2,3,5,6-TETRAMETHYL-*p*-BENZOQUINONE[b] (DUROQUINONE) WITH VINYL MONOMERS

Expt no.	Monomer	Time, hr	Solvent[c]	Polymeric product	Yield, %	Reduced viscosity (solvent)	Analysis, %	
							C	Other
1	Styrene	72	Monomer	Yes	9[d]	0.10 (DMF)	92.10	
2	Acrylonitrile	16	Monomer	Yes	85	0.86 (DMF)	64.74	23.45[e]
3	Vinyl acetate	72	Monomer	No				
4	Ethyl acrylate	72	Monomer	Yes	22[d]	0.08 (benzene)	59.71	
5	Methyl α-chloroacrylate	42	Monomer	Yes	84	0.75 (DMSO)	39.24	28.70[f]
6	*N*-Vinylcarbazole	88	Chlorobenzene	No				
7	Vinyl isobutyl ether	42	Momoner	No				
8	Vinylidene chloride	42	Momoner	Yes	24[g]	*h*	24.06	57.29[f]
9	2-Chlorostyrene	42	Monomer	Yes	67[d]	0.15 (benzene)	69.82	25.15[f]

[a] Reactions conducted at 70° with 1.3 mol % benzoyl peroxide (based on duroquinone). [b] Duroquinone recrystallized thrice for ethanol–water and sublimed twice. [c] When monomer is referred to as solvent, 4 equiv of monomer per equivalent of duroquinone was employed; when a special solvent is used, the quinone and monomer are in a 1:1 molar ratio. [d] Polymer contained less than 5 wt % quinone and yield calculated on homopolymer of vinyl monomer. [e] Presented as elemental nitrogen analysis. [f] Presented as elemental chlorine analysis. [g] Copolymer contained 6:1 mol ratio of vinylidene chloride–duroquinone. [h] Copolymer insoluble in DMSO and DMF.

porated quinone. Under reaction conditions, the naphthoquinone appeared to have a pronounced retarding influence upon chain growth of poly(*p*-methoxystyrene), 2-chlorostyrene, and *N*-vinylcarbazole, but little if any upon the polymerization of methyl α-chloroacrylate.

Reaction with vinyltoluene (expt no. 11) afforded a very low yield of polymeric material of reduced viscosity 0.06 (benzene). A 2:1 molar ratio between styrene and quinone, respectively, was established by elemental chlorine analysis.

Reaction of 2,3,5,6-Tetramethyl-*p*-benzoquinone (Duroquinone) (E_0 = 0.47) with Vinyl Monomers. 2,3,5,6-Tetramethyl-*p*-benzoquinone (duroquinone) was treated with a series of vinyl monomers at 70° and the results are tabulated in Table III. A 4:1 molar ratio of monomer–quinone was utilized for bulk reactions, whereas a 1:1 ratio was used for reactions involving a special solvent.

The bulk reactions of duroquinone with vinyl acetate (expt no. 3) and with vinyl isobutyl ether (expt no. 7) did not produce any isolable polymeric products. Reaction with *N*-vinylcarbazole (expt no. 6) in the presence of chlorobenzene diluent afforded a deep coloration but no isolable product.

Bulk reactions with styrene (expt no. 1), ethyl acrylate (expt no. 4), and 2-chlorostyrene (expt no. 9) afforded variable yields of low molecular weight polymers. Reaction with acrylonitrile (expt no. 2) gave a high yield of a high molecular weight polymer. However, elemental analysis showed each of these materials to consist largely of the homopolymers of the vinyl nonomer with less than 5 wt % of incorporated quinone.

The bulk reaction with methyl α-chloroacrylate (expt no. 5) provided an excellent yield of poly(methyl α-chloroacrylate) with very little incorporated quinone. The reduced viscosity of the once-purified polymer, dissolved overnight in dimethyl sulfoxide (DMSO) at 60° and precipitated by addition of methanol, was 0.75 (DMSO). A second precipitation, however, lowered the reduced viscosity to 0.28. Although the quinone had been incorporated to only a minor extent, it may have served as weak points in the polymer chain and allowed degradation by DMSO.

Vinylidene chloride copolymerized in bulk with duroquinone to yield a copolymer of 6:1 molar ratio of vinylidene chloride–duroquinone (expt no. 8). After an initial benzene wash, the copolymer was dissolved in dimethylformamide (DMF), precipitated by pouring the DMF solution into methanol, and dried *in vacuo* at 50°. However, the dried material was insoluble in DMF or any other organic solvent. Cross-linking had apparently occurred during purification and drying, possibly *via* cleavage and recombination of monomer–quinone linkages.

Conclusion

We have established that 2,3-dichloro-1,4-naphthoquinone, 2,3,5,6-tetramethyl-*p*-benzoquinone, and 1,4,5,8-tetrachloroanthraquinone can be made to undergo copolymerization reactions with certain vinyl monomers under specific experimental conditions. However, only the anthraquinone exhibited a general tendency to copolymerize with a wide variety of vinyl compounds. Although we did not find a direct method for the preparation of aromatic–aliphatic polyethers as originally envisioned, we have prepared a number of new polymers and pointed the way to the preparation of copolymers containing various anthraquinone residues.