Linear, soluble poly(bismethylene hydroquinone), a ladder polymer: synthesis and characterization

Xian-Tong Bi* and Morton H. Litt
Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, USA

(Received 27 January 1987; accepted 8 June 1987)

A route to prepare a soluble linear ladder of poly(bismethylene hydroquinone) was developed. 2,3,5,6-Tetramethylol hydroquinone was reacted with hydroquinone in sulpholane with acid catalysis. Gel formation was prevented by removing the water generated during the condensation, and by preventing oxidation of the polymer during reaction. Polymers with intrinsic viscosities as high as 5.0 were obtained; viscosity depended on the mole ratio of the starting materials and the reaction conditions. Polymer structure was characterized by Fourier transform infra-red spectroscopy, nuclear magnetic resonance spectroscopy, polarizing microscopy and X-ray diffraction.

(Keywords: ladder polymer; hydroquinone; oxidation–reduction; liquid crystal; crystalline)

INTRODUCTION

Polymeric quinones are an interesting class of materials which have attracted study because of their ability to behave as oxidation–reduction systems[1–13]. Phenolic resins are well known[14–18], and conducting polymers can also be made from phenol-formaldehyde resins[19] but high-molecular-weight linear polymer is very difficult to make. Polyquinones are similar to phenolic resins on this point. In a recent study, the reaction of hydroquinone with trioxane was investigated[20]. The product was a crosslinked insoluble poly(bismethylene hydroquinone). In this paper, a new reaction is reported which produces a linear, soluble poly(bismethylene hydroquinone), a ladder polymer, with high instrinsic viscosity.

EXPERIMENTAL

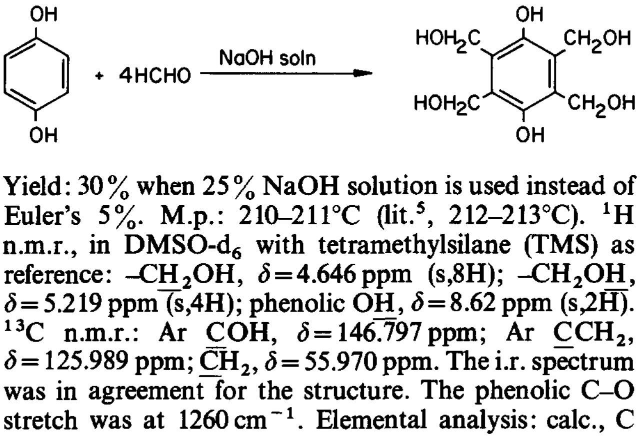
Synthesis of poly(bismethylene hydroquinone)

Starting materials. Hydroquinone (HQ), 37% (w/w) water solution of formaldehyde, toluene sulphonic acid, cyclohexane and methyl cyclohexane were obtained from Fisher Scientific Co. and used as received.

Sulpholane was obtained from Eastman Kodak Co. Some 10% (w/w NaOH pellets were put in the sulpholane for 24 h. The sulpholane was decanted and distilled twice from 10% (w/w) NaOH pellets under vacuum (b.p. 87°C/0.2 mmHg). At the end of the second distillation, 1 ml of sulpholane did not produce any colouration in 5 min with 1 ml of conc. H_2SO_4. The purified sulpholane was stored under dry nitrogen.

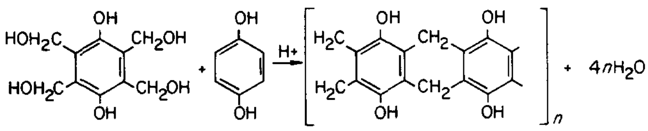
Molecular sieves, 4 Å, obtained from Fisher Scientific Co., were baked at > 500°C for 4 h before use.

Preparation of 2,3,5,6-tetramethylol hydroquinone (TMHQ). We improved on the method of Euler *et al.*[21]



Yield: 30% when 25% NaOH solution is used instead of Euler's 5%. M.p.: 210–211°C (lit.[5], 212–213°C). ^1H n.m.r., in DMSO-d_6 with tetramethylsilane (TMS) as reference: $-\underline{CH_2}OH$, $\delta = 4.646$ ppm (s,8H); $-CH_2O\underline{H}$, $\delta = 5.219$ ppm (s,4H); phenolic $O\underline{H}$, $\delta = 8.62$ ppm (s,2H). ^{13}C n.m.r.: Ar $\underline{C}OH$, $\delta = 146.797$ ppm; Ar $\underline{C}CH_2$, $\delta = 125.989$ ppm; $\underline{C}H_2$, $\delta = 55.970$ ppm. The i.r. spectrum was in agreement for the structure. The phenolic C–O stretch was at 1260 cm^{-1}. Elemental analysis: calc., C 52.17, H 6.13; found, C 52.19, H 6.17.

Polycondensation of 2,3,5,6-tetramethylol hydroquinone (TMHQ) and hydroquinone (HQ). A typical reaction is described below.



0.460 g (0.00200 mol) of TMHQ was placed in 15 ml of redistilled sulpholane. The mixture was warmed to 150°C to dissolve the TMHQ and then cooled to ~80°C. It was added to a 200 ml pressure bottle or 100 ml pressure tube (Arthur H. Thomas Co.) containing from 0.220 g (0.00200 mol; equimolar with TMHQ) to 0.264 g (0.00240 mol; 20% excess) of HQ, and 0.0460 g of toluene sulphonic acid (TSA) in sulpholane. The total amount of sulpholane used depended on the desired concentration of monomers, 2% or 5%. Then 2 g of 4 Å molecular sieves per gram of monomer was added.

Reaction vessel. Three different series of reaction

---

* Visiting scholar from the Institute of Chemistry, Academia Sinica, Beijing, China

0032-3861/87/132346–07$03.00

Table 1 Action of molecular sieves to prevent gelation

HQ/TMHQ (mol ratio)	Concentration (wt%)	Reaction temp. (°C)	Reaction time (h)	Molecular sieves[a] (used or not)	Polymer final state[b]
1.000	5	120	0.5	no	G
			4	yes	S
1.040	2	120	3	no	G
			4	yes	S
1.010	2	120	12	yes	S
1.005	2	120	4	no	G
		120	4	yes	S
		150	4	yes	S
		170	4	yes	S
1.005	5	150	6	yes	S
1.003	2	120	12	yes	S
		170	20		
		130	12	yes	S
		170	20		

[a] 2 g of 4 Å type molecular sieves per 1 g monomer
[b] S = polymer soluble; G = polymer gelled

conditions were studied, and they were run in two different types of reaction vessel (see *Table 2*):

For series I, a 200 ml pressure bottle (Thomas Scientific Co.) sealed by a special glass stopper was used. Dry N_2 was blown into the vessel for 10 min before it was sealed.

For series II, a 100 ml pressure tube (Thomas Scientific Co., PVC-coated) with an aluminium cap with a vacuum-tight needle valve sealed with a Buna-N O-ring was used. It was evacuated before reaction.

For series III, the same pressure tube was used. It was evacuated, charged with dry N_2 and then reacted.

Reaction and post-treatment. The reaction vessel was put in a silicone oil bath which was preheated and controlled at the desired temperature (120, 130, 150 or 170°C) for the desired time interval. The reactants and solvent were stirred during reaction, using a magnetic stirrer. After the reaction, the solution was cooled. The large particles of molecular sieves settled to the bottom of the reaction vessel. The polymer solution was decanted and centrifuged for further separation of some fine powder from abraded molecular sieves. The polymer was precipitated by adding a mixture of 50 ml dimethyl formamide (DMF) and 150 ml distilled water. The precipitate was centrifuged. Then the polymer was redissolved in 50 ml DMF, reprecipitated by adding 150 ml of distilled water and centrifuged. This was repeated five times. The polymer, dried overnight at room temperature under vacuum, was used for most of the characterizations. Exceptions are noted. Elemental analysis: no. 16 (*Table 2*), C 65.03, H 4.69, S 1.94, ash 0.037; no. 2 (*Table 2*), C 64.11, H 4.63, S 0.78.

Characterization

Solubility. Wet polymers with intrinsic viscosity less than 0.5 dl g^{-1} were soluble in acetone, DMF, dimethyl acetamide (DMAc), dimethyl sulphoxide (DMSO), N-methyl pyrrolidone and sulpholane. Wet polymers with intrinsic viscosity 0.5–5.0 dl g^{-1} were insoluble in acetone but soluble in the rest of the solvents listed above.

Dried polymers with intrinsic viscosity less than 0.2 dl g^{-1} were soluble in DMF, DMSO, DMAc, sulpholane and N-methyl pyrrolidone. Dried polymers with intrinsic viscosity more than 0.2 dl g^{-1} were only slightly soluble in sulpholane, DMF, DMSO and DMAc but remained soluble in N-methyl pyrrolidone.

Intrinsic viscosity. For the dried polymers, flow times for 0.4–1.0% (w/v) DMF solutions were measured in an Ubbelohde dilution viscometer at 25 ± 0.1°C. Data were taken at five concentrations.

Since the high-viscosity polymers became almost insoluble when dried, solutions for viscosity measurement were prepared by centrifuging the reaction mixture and diluting the supernatant polymer solution to about 0.7% (w/v) with sulpholane; viscosity was measured at 30 ± 0.1°C. Data were taken at five concentrations. Concentration was calculated based on the initial weight of polymer in the solution.

FTi.r. spectra. Infra-red spectra were obtained on a Digilab Model FTS-14 Fourier transform spectrophotometer. Samples were pressed in KBr pellets. Each spectrum was recorded at a resolution of 8 cm^{-1} with a total of 10 scans.

N.m.r. spectra. ^{1}H and ^{13}C solution n.m.r. spectral determinations were run at 187 MHz for ^{1}H and 47 MHz for ^{13}C using a Varian XL-200 spectrometer. TMHQ was measured in DMSO-d_6 at 10% concentration (w/v) with a TMS reference. DMSO-d_6 also provided an internal lock signal for the ^{13}C n.m.r. The instrumental conditions were: pulse signal, 90°; pulse delay, 10 s; and number of transients, 500.

The ^{13}C solid-state CP/MAS n.m.r. spectra were recorded at 37.7 MHz with a modified Nicolet NT-150 spectrometer equipped with a cross-polarization accessory. Radiofrequency amplifiers delivering 550 W at 150 MHz and 1000 W at 37.7 MHz were adjusted to satisfy Hartmann–Hahn conditions[22] at ~64 kHz. In all cross-polarization experiments, the contact time was 1 ms, and the delay between successive pulse sequences was 2 s. The Andrew beam type spinners were constructed from polyoxymethylene (Delrin), and were spun at about

Table 2 Intrinsic viscosity of soluble poly(bismethylene hydroquinone)

Reaction series number[a]	Polymer run number	Concentration of starting materials in sulpholane, (wt%)	HQ/TMHQ (mol ratio)	Temp./time (°C/h)	Soluble (%)	$[\eta]$ (dl g^{-1})	Solvent[b]	Conversion (%)
I	1	2	1.20	120/2.5	100	0.06	D	
II	2	2	1.02	120/4	100	0.092	D	
	3			120/8	100	0.178	D	
	4			120/12	100	0.238	D	
III	5	2	1.01	120/4[c]	100	0.232	D	
	6			120/12[d]	40	0.470	D	
	7			150/8	100	0.380	S	
	8			150/12	100	0.80	S	
III	9	2	1.005	170/12	30	5.0	S	
III	10	2	1.003	130/4	100	0.21	S	66[e]
	11			130/10	100	0.24	S	77[e]
	12			130/15	100	0.42	S	82[e]
	13			130/15 170/6	100	0.63	S	99
	14			130/15 170/12	100	0.95	S	99.1
	15			120/12 170/6	100	0.65	S	95.4
	16			120/12 170/20	100	1.20	S	99.3
III	17	2	1.000	120/4	100	0.246	D	
III	18	5	1.010	120/5	100	0.30	S	
III	19	5	1.005	150/6	100	0.50	S	
	20			120/4 150/4 170/4	100	3.0	S	
III	21	5	1.000	120/4	16	0.252	D	
	22			150/2	100	0.56	S	
	23			150/2.5	64	1.00	S	
	24			150/5	–	gelled		

[a] I: in pressure bottle (sealed); II: in pressure tube (vacuum); III: in pressure tube (sealed), with molecular sieves

[b] D = DMF; S = sulpholane

[c] 2 ml of cyclohexane was added to generate pressure at the reaction temperature to prevent oxidation

[d] 2 ml of methylcyclohexane was added

[e] Low conversion is due to some loss of soluble polymer during wash-up

3.5 kHz. The Delrin peak (89 ppm) was used as a reference.

X-ray diffraction. Flat-plate X-ray diffraction patterns were taken on a Statton camera with Ni-filtered Cu Kα radiation. Calcium fluoride was used for calibration.

Polarizing microscopy. Wet polymer was dissolved in a sulpholane/acetone mixture and filtered through a 0.5 μm filter. The solution on a microscope slide was evaporated under vacuum at room temperature. Photographs were taken at a magnification of 400 × using a Zeiss polarizing transmission microscope.

Elemental analyses. These were done by the Galbraith Laboratories, Knoxville, Tennessee, USA.

RESULTS AND DISCUSSION

Chemical structure of TMHQ

^{1}H and ^{13}C n.m.r. spectra show that we have the desired compound. Elemental analysis shows that it can be obtained in high purity.

Polymer preparation

Usually, a linear polymer cannot be prepared through polycondensation of two tetrafunctional monomers such as TMHQ and HQ. This is exemplified by the reaction of HQ with formaldehyde, where crosslinked polymer was obtained[20].

The rationale for using TMHQ is given below. When formaldehyde is used, reaction is random, and formaldehyde could have already added to a position on a hydroquinone which is situated to react with a methylol group to close the ring. However, when TMHQ is used, once one methylol has reacted with HQ, the second is positioned to react with a free HQ site and to cyclize. As will be shown by the data, the cyclization reaction is slow compared to the first addition. However, steric factors seem to lower the reactivity of such methylol groups, so they eventually cyclize.

One problem may be reversion, the conversion of a methylol group to formaldehyde, which can then add to any HQ position and create branch points. Reversion seems to be facilitated by water, so the reaction was kept anhydrous by the addition of molecular sieves.

The main factor for preventing gel formation is removing the water which is generated during the condensation (*Table 1*).

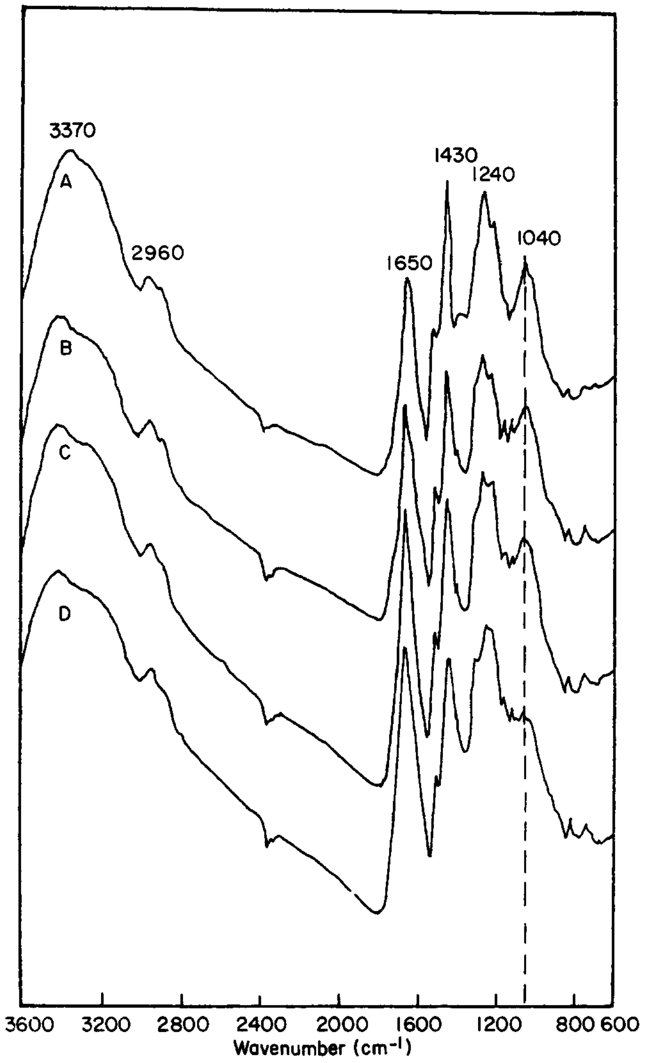


Figure 1 *FT*i.r. spectra of poly(bismethylene hydroquinone): A, no. 10; B, no. 11; C, no. 12; D, no. 13 (*Table 2*)

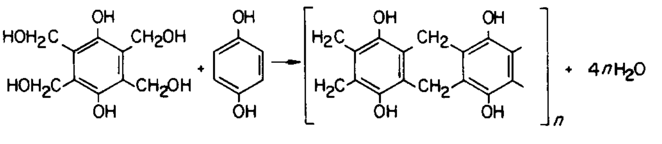
High-intrinsic-viscosity linear polymer

In order to get useful polymer, a high-molecular-weight, soluble polymer has to be made. We used intrinsic viscosity as a measure of molecular weight. High-pressure g.p.c. measurements (in DMF) consistently showed peaks at the exclusion limit of the columns; the polymers may be associated in DMF.

After heating at 120°C (or 130°C) for 4–12 h, the intrinsic viscosity of the polymer was 0.10–0.25 dl g^{-1}. Both the intrinsic viscosity and the conversion of the polymers increased further by heating at high temperature (*Table 2*). There was a slight tendency to gelation at reactant ratios very close to 1.000. However, intrinsic viscosities as high as 3 were obtained relatively easily with no gelation, and even higher values were found for the soluble fractions of partly gelled materials. As will be discussed, higher temperatures and longer times result in more complete reaction. The fully reacted structure is regular and the polymer can crystallize. We do not know if the gelation observed at 150–170°C is due to partial crystallization or crosslinking.

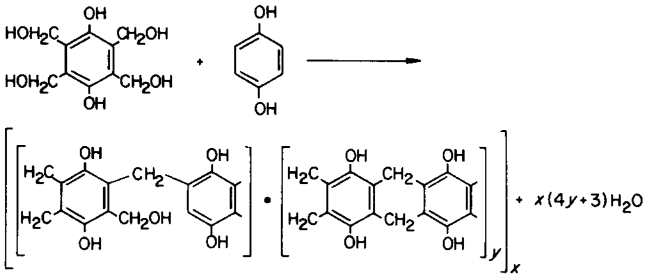
Chemical structure of the polymer

Polycondensation which gives high-viscosity soluble polymer must approximate to the following:



(I) (II) (A)

However, *FT*i.r. spectra (*Figure 1*) show that the condensation reaction goes through intermediates which retain the CH_2OH group. Possible structures are the following:



(B)

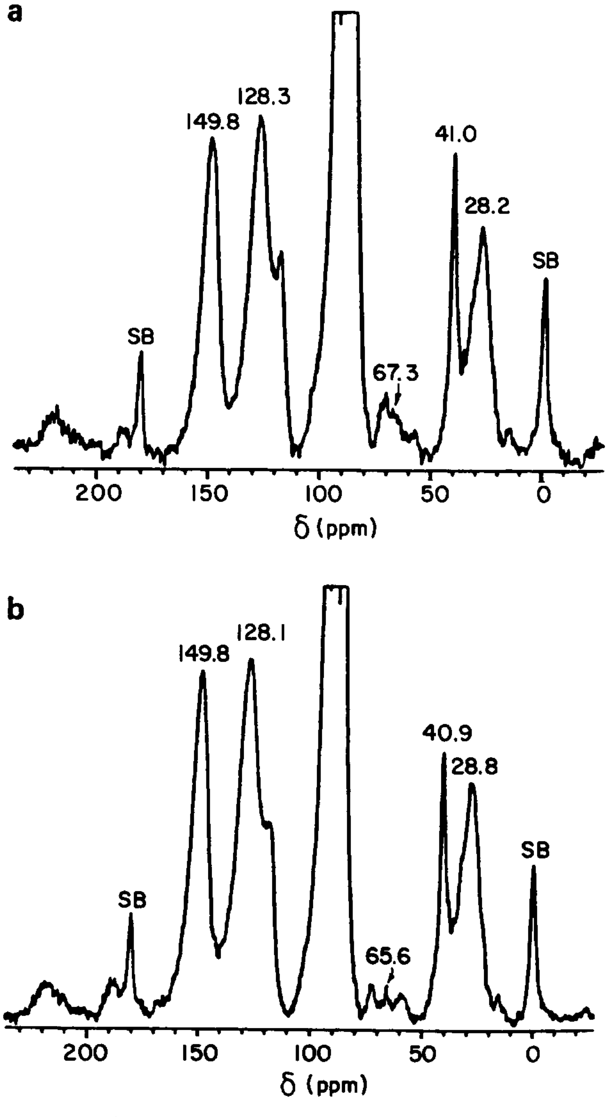


Figure 2 ^{13}C solid-state n.m.r. of poly(bismethylene hydroquinone), HQ/TMHQ = 1.20 (mol ratio): (a) 120°C/2.5 h; (b) 120°C/5 h. Peak at 41 ppm due to sulpholane

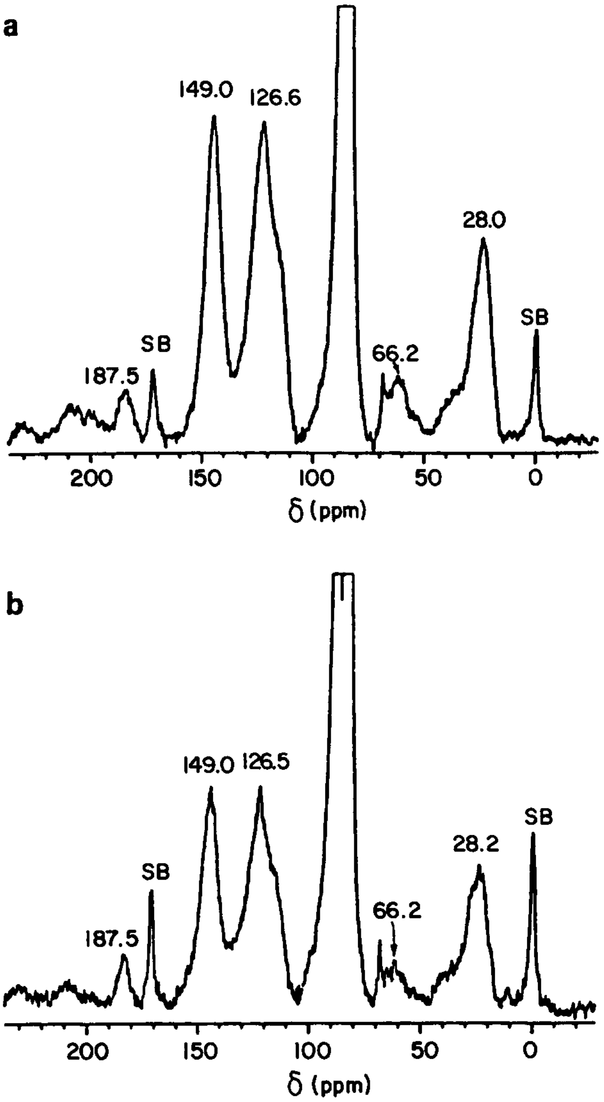


Figure 3 ^{13}C solid-state n.m.r. of poly(bismethylene hydroquinone), HQ/TMHQ = 1.10 (mol ratio): (a) 120°C/2 h; (b) 120°C/2 h (1st step), 150°C/2 h (2nd step)

The CH_2OH peak at $1040\,cm^{-1}$ decreases with increasing temperature and reaction time (*Figure 1*) until the final product, structure [A], is reached. It is exemplified by spectrum D in *Figure 1*, which shows almost no CH_2OH absorption. *Figure 1* also shows quinone absorption at $1650\,cm^{-1}$, $-CH_2-$ bend at $1430\,cm^{-1}$ and aromatic C–O stretch at 1200 and $1240\,cm^{-1}$.

The solution colour after reaction is brown, showing that some kind of oxidation is occurring even under an N_2 atmosphere. This is reflected by the quinone absorption. However, the solid-state n.m.r. spectra discussed later suggest that only a small amount of quinone may be present.

Element analyses were run on samples 16 and 2 (*Table 2*) (see 'Experimental' for data). For sample 16, this gave a polymer of the following composition;

$$C_{8.00}H_{5.35}O_{2.00}{\cdot}0.55(H_2O){\cdot}0.094(C_4H_8SO_2)$$

with an exact fit for C, H and S. Sulpholane remains even after much washing and water may also be trapped. Also, any unreacted methylol groups would show up as H_2O. The postulate that there was no oxidation (six H per repeat) gives a fit with elemental analysis that is just at the limits of acceptability. In any case, there could be some oxidation which lowers the hydrogen content during the work-up as well as during polymerization.

Run 2 should be less condensed than run 10, whose i.r. spectrum is given in *Figure 1* (trace A), since it was reacted

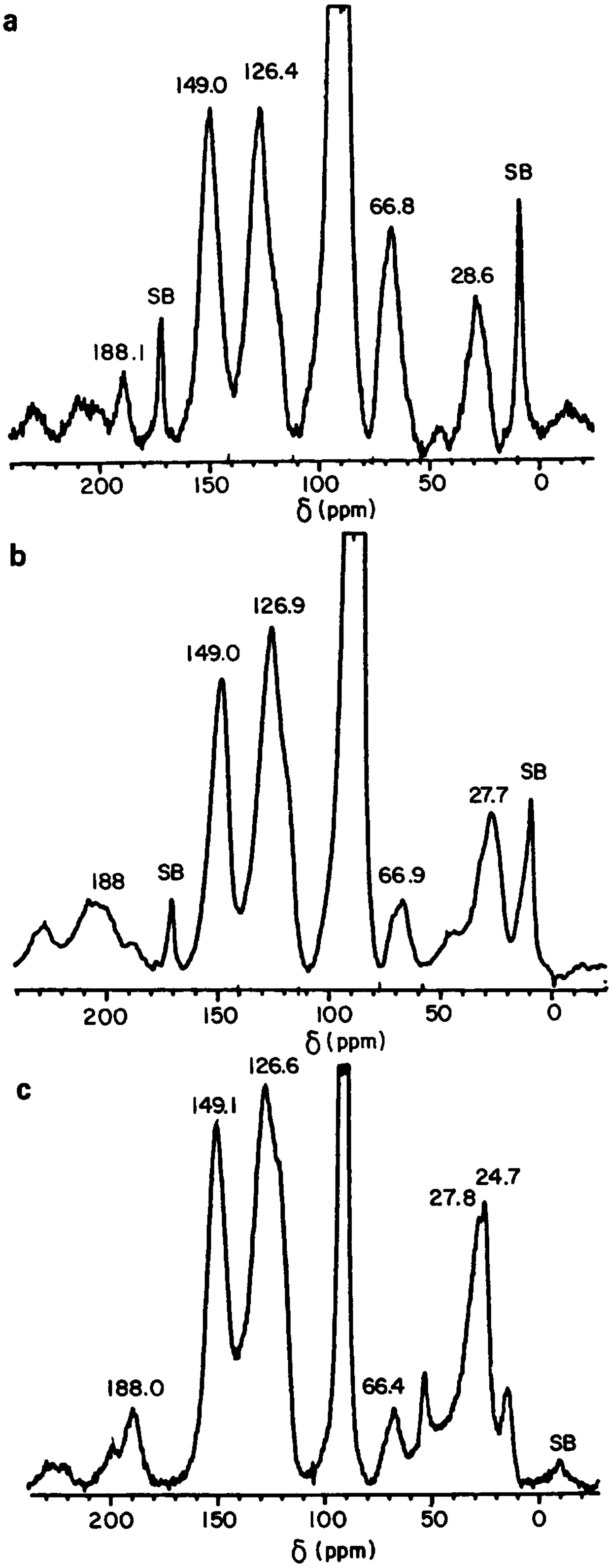


Figure 4 ^{13}C solid-state n.m.r. of poly(bismethylene hydroquinone): (a) no. 5; (b) no. 8; (c) no. 20 (*Table 2*)

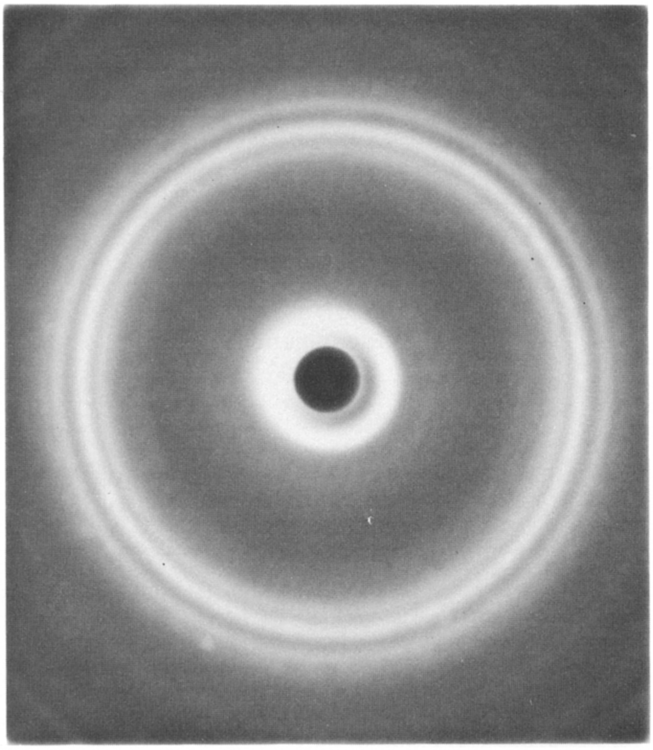


Figure 5 X-ray diffraction pattern of crystalline poly(bismethylene hydroquinone)

under less severe conditions. There is a large peak at 1040 cm^{-1} due to remaining CH$_2$OH groups. Its elemental analysis, given in 'Experimental', comes out as:

$$C_{8.00}H_{5.04}O_2{\cdot}0.83(H_2O){\cdot}0.037(C_4H_8SO_2)$$

In this case, much of the 'water' should be unreacted methylol groups. When a polymer synthesized under identical reaction conditions was analysed by bromination[23], it was found that there were about 0.37 CH$_2$OH groups per C$_8$ repeat.

^{13}C solid-state n.m.r. spectra show that when the mole ratio of HQ/TMHQ was 1.20 or 1.10, the –CH$_2$OH peak at 66.9 ppm disappeared rapidly (*Figures 2* and *3*). When the mole ratio of HQ/TMHQ was decreased to 1.01, the methylol groups reacted more slowly. Therefore, the reaction temperature and time had to be increased in order to complete ring closure (*Figure 4*).

The area ratios of the peak at 27.7–28.6 ppm (–$\underline{C}$H$_2$–) to that at 66.4–66.9 ppm (–$\underline{C}$H$_2$OH) of runs 5, 8 and 20 (*Table 2*), given in *Figures 4a*, *4b* and *4c*, are equal to 0.78, 3.41 and 4.9 respectively. CH$_2$OH decreases with increased temperature and time of reaction. These ratios are low and imply relatively little ring closure. In fact, for a ratio of 0.78, $\bar{X}_n$ would be about 5 at the maximum. This is incompatible with the intrinsic viscosity found, 0.232. See the following discussion for a possible rationale to explain this.

All of the ^{13}C solid-state n.m.r. spectra show Ar $\underline{C}$OH at 149.0 ppm, Ar $\underline{C}$–CH$_2$ at 126.6 ppm and –$\underline{C}\underline{H_2}$– at 28 ppm. Peaks for these groups appear in the *FT*i.r. spectra. Carbonyl carbon resonances due to quinone formation appear at 187.9 ± 0.2 ppm. The peak area is very small compared to that of the phenolic carbon, while in the *FT*i.r. spectra (*Figure 1*) the peak is quite large. There are two possibilities for this. First and most obvious, the quinone absorption in the i.r. has a large extinction coefficient. It is prominent even though only a small fraction of the polymer is oxidized. Secondly, the quinone groups are really present but coupled to hydroquinones to form semiquinones and exchange electrons with other semiquinones. This would relax the carbons involved in this exchange so rapidly that they would not be visible using ^{13}C solid-state n.m.r. At present, we are not certain which possibility is more important for this case. When the polymer is oxidized, the second phenomenon becomes important[23]. However, the relatively small area ratio of –$\underline{C}$H$_2$– to –$\underline{C}$H$_2$OH implies that the effect may be operating here also. We know that we have almost complete ring closure in our best-made polymers because they can crystallize well, as discussed later.

X-ray diffraction

The soluble poly(bismethylene hydroquinone) reacted at 170°C can be crystallized by gradually evaporating the solvent.

From a well reacted polymer, sample no. 16 (*Table 2*), 14 diffraction lines were found (*Figure 5*). The *d*-spacings are listed in *Table 3*.

As can be seen from *Figure 5*, there is very little amorphous scattering. The rings are reasonably sharp. All the molecular sieve particles were removed by centrifugation and filtration. Powder patterns of sieves show no identity with the polymer *d*-spacings.

Many unit cells can be found to fit the data, since there are two very large dimensions. However, none seem to make sense for ladder polymer packing. We are trying to make oriented fibres to study this more thoroughly.

Optical characterization

Optical photomicrographs of a crystalline polymer taken using polarized light are shown in *Figure 6*. The same region is shown in both photographs, with the polarization shifted by 45°. One can see that, while the morphology seems spherulitic at the right side of the photograph, in addition, large regions (see upper and centre left for the best example) extinguish as a unit. The macroscopic regions of uniform orientation imply initial liquid-crystal aggregation, which later crystallizes as solvent continues to evaporate.

Table 3 Observed *d*-spacings from powder pattern of crystallized sample no. 16 (*Table 2*)

Number	*I*	*d* (Å)
1	w	22.1
2	ss	18.0
3	w	10.96
4	w	5.90
5	m	4.865
6	s	4.595
7	m	4.182
8	w	4.047
9	w	3.950
10	vw	3.547
11	w	3.420
12	vw	3.271
13	vw	2.982
14	m	2.826

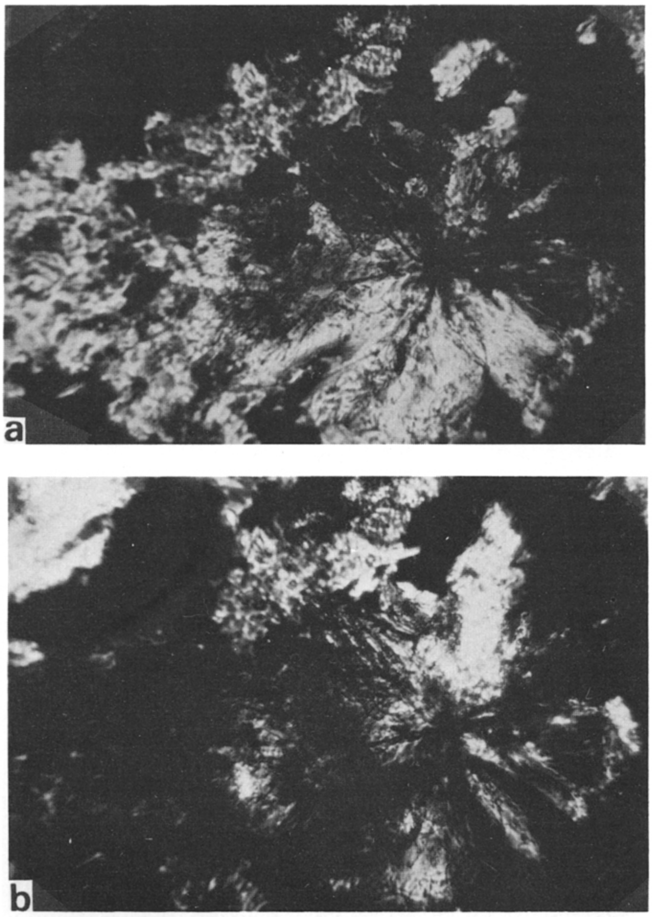


Figure 6 Cross-polarized light microscopy of crystalline poly(bismethylene hydroquinone): (a) polarizer at 0°; (b) polarizer at +45°

CONCLUSIONS

We have synthesized a new soluble ladder polymer, poly(bismethylene hydroquinone), which was obtained by the polycondensation of 2,3,5,6-tetramethylol hydroquinone with hydroquinone under conditions where water and oxygen were rigorously excluded. The final polymer obtained after heating at 170°C could be crystallized to a high degree of crystallinity. This shows that a regular structure was obtained, which supports our conclusions that we have extensive ring closure.

ACKNOWLEDGEMENTS

This work was supported by the Department of Energy under Grant No. 342-9501. We thank Ms M. Zaper for the ^{13}C solid n.m.r. determinations.

REFERENCES

1 Cassidy, H. G. *J. Am. Chem. Soc.* 1949, **71**, 402
2 Updergraff, I. H. and Cassidy, H. G. *J. Am. Chem. Soc.* 1949, **71**, 407
3 Manecke, G. *Z. Electrochem.* 1953, **58**, 189
4 Ezrin, M. and Cassidy, H. G. *Ann NY Acad. Sci.* 1953, **57**, 79
5 Manecke, G. *Z. Electrochem.* 1954, **58**, 369
6 Cassidy, H. G. *Proc. Nat. Acad. Sci., USA* 1952, **38**, 934; US Patent 2700029, 1955
7 Manecke, G., Bahr, Ch. and Reiech, Ch. *Angew. Chem.* 1959, **17**, 646
8 Dalibor, H. *Chem. Ber.* 1958, **91**, 1955
9 Hunt, S. E. and Lindsey, A. S. *Chem. Ind.* 1961, 1273
10 Quisenberry, R. K. *Diss. Abstr.* 1961, **22**, 77
11 Peover, M. E. and Lindsey, A. S. *Chem. Ind.* 1961, 1272
12 Peover, M. E. and Lindsey, A. S. *Chem. Ind.* 1961, 1273
13 Hunt, S. E. and Lindsey, A. S. *J. Chem. Soc.* (*4*) 1962, 4550, 4558
14 Carswell, T. S. 'Phenoplastics', Interscience, New York, 1947
15 Martin, R. W. 'The Chemistry of Phenolic Resins', New York, 1956
16 Megson, N. J. L. 'Phenolic Resin Chemistry', Butterworth, London, 1958
17 Coggeshall, N. *J. Am. Chem. Soc.* 1950, **72**, 2836
18 Ambellang, A. and Binder, J. *J. Am. Chem. Soc.* 1953, **75**, 947
19 Tanaka, K., Ohzeki, K. and Yamabe, T. *Synthetic Metals* 1984, **9**, 41
20 Dalal, V. F., Litt, M. H. and Rickert, S. E. *J. Polym. Sci.* 1985, **23**, 2659
21 Euler, H. V., Adler, E. and Gie, G. J. *Ark. Kem., Mineral. Geol.* 1940, Ser. **B14**(9), 1
22 Hartmann, S. and Hahn, E. *Phys. Rev. B* 1962, **12**, 2042
23 Dalal, V. F., Bi, X. T., Daroux, M. L., Litt, M. H. and Rickert, S. E. *J. Electrochem.* in press