Gel chromatographic investigation of *p*-benzoquinone and styrene products copolymerized in the presence of $BF_3{\cdot}OEt_2$

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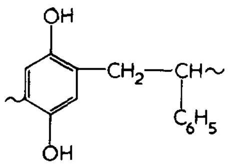
The molecular weight distribution of copolymers of *p*-benzoquinone and styrene was studied by g.p.c.. It was shown that the products synthesized have low molecular weights and narrow *MWD*. *p*-Benzoquinone was found to be a copolymer macromolecule regulator.

Keywords Cationic copolymerization; copolymer of *p*-benzoquinone; styrene; molecular weight distribution; hydroquinone links; molecular weight regulator; gel permeation chromatography

INTRODUCTION

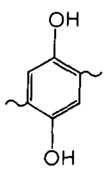
It was shown earlier[1,2] that *p*-benzoquinone (BQ) during copolymerization with styrene (St) in the presence of cationic initiators has a significant effect on the rate. The main reaction product is an oligomer having hydroquinone and styrene links[2,3]:



A cationic mechanism of BQ–St copolymerization is proposed on the basis of investigation of the kinetics[2] and products[3]. The molecular complex of comonomers is prominent for this mechanism.

It is established[4] that this cationic copolymerization is accompanied by side-reactions resulting in a small amount (5–7%) of hydroquinone and oligomer. The nature (solubility, colour and composition) of the latter is different from that of BQ–St copolymer.

The results of the chemical and spectral analyses, determination of hydroxyl and hydroquinone groups, and comparison with the characteristics of *p*-benzoquinone polymer obtained by a known procedure[5] allow us to conclude that the oligomer consists of 2,5-substituted hydroquinone links, i.e. it is oligohydroquinone. As BQ is



incapable of homopolymerization in the presence of cationic initiators at 0°–40°C[6] (i.e. under conditions of copolymerization with St), this reaction does not lead to oligohydroquinone formation in the BQ–St copolymerization process. Based on the dehydrogenating activity of BQ in the presence of Lewis acids we assume that during the process of cationic copolymerization, dehydrogenation between quinone and hydroquinone links of copolymer occurs. It seems that the reaction results in semiquinone radical formation. The radicals form hydroquinone and oligohydroquinone by disproportionation and recombination reactions[4]. The contribution of this reaction varies depending on conditions.

Therefore it was interesting to study, using g.p.c., the composition and molecular weight distribution (*MWD*) of the BQ–St copolymerization products made in the presence of boron trifluoride etherate ($BF_3{\cdot}OEt_2$) and to examine the effect of BQ on the *MWD* characteristics of copolymers.

EXPERIMENTAL

The synthesis and isolation of the BQ–St copolymerization products were carried out according to published methods[3]. The synthesis conditions for BQ–St copolymers, values of number average molecular weights and polydispersity coefficient ($\bar{M}_w/\bar{M}_n$) are listed in *Table 1*. Before carrying out g.p.c. analyses, the copolymerization products were separated into two fractions by treatment with benzene. The soluble fraction consists of BQ–St copolymer, and the insoluble one of hydroquinone, quinhydrone and polyhydroquinone.

The g.p.c. investigation was carried out on a 'Waters' instrument provided with styrogel columns with 200, 500 and 1000 Å porosity. Tetrahydrofuran (THF) was used as eluent; the feed rate was 1.0 to 1.1 ml min^{-1}, temperature 25°C. An aliquot of the sample to be analysed (0.1 to 0.2 wt%) was introduced over a 1 minute period.

The apparatus was calibrated by means of polystyrene

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standards of narrow *MWD*. The calibration of the polyhydroquinone samples was effected by a published method[7]:

$$V_R = C_1 - C_2 \log \bar{M}$$

where $C_1 = 39.01$ and $C_2 = 6.76$.

Handling of the chromatograms and calculation of the distribution parameters were carried out according to the formulae:

$$\bar{M}_w = \Sigma M_i \cdot W_i \quad \text{and} \quad \bar{M}_n = 1/\Sigma W_i/\bar{M}_i$$

where W_i is the weight fraction of the *i*th fraction which has been defined from the ratio of the *i*th section of the chromatogram to the overall area, and M_i is the molecular weight of the *i*th fraction.

Formulae with $A_1 = 0.98$ and $A_2 = 1.02$ link the true values of molecular weights (M^t) and values obtained after chromatogram handling[8]:

$$\bar{M}^t_w = \bar{M}_w \cdot A_1 \quad \text{and} \quad \bar{M}^t_n = \bar{M}_n \cdot A_2$$

In order to check the accuracy of the polystyrene calibration for the *MWD* parameters of BQ–St copolymers the values of the number average molecular weights were determined by a known method[9]. A good correlation was established between $\bar{M}_n$ values of copolymers determined by two methods, thereby the accuracy of calibration was confirmed.

Figure 1 shows typical g.c. curves of the byproducts of BQ–St copolymerization. They consist presumably of quinhydrone and hydroquinone (see *Table 2*). In this fraction a small amount (8–14 wt%) of polyhydroquinone was found. On increasing the initial concentraion of the catalyst in the reaction mixture the amount of hydroquinone in the byproducts increases and that of quinhydrone and polyhydroquinone decreases. Thereby a decrease in molecular weight of polyhydroquinone is observed with increase in initial concentration of the catalyst.

It should be noted that the polyhydroquinone has a low degree of polymerization and a narrow *MWD*.

G.p.c. analyses of the copolymer fraction indicate that it ranges from di- and trimers to polymers of molecular weight up to 3000 (see *Figure 2*). But tetra- and pentamers

Table 1 Conditions of copolymerization of styrene and *p*-benzoquinone in the presence of $BF_3.OEt_2$ and molecular weights of reaction products. $[St]_0 + [BQ]_0 = 0.70$ mol l^{-1}, $T = 20°C$; Time, 1 h, $[Cat]_0 = 0.003$ mol l^{-1}

No.	St : BQ, mole %	*MWD* (from g.p.c.) $\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
1	100 : 0	6700	1910	3.51
2	98 : 2	3370	1640	2.31
3	90 : 10	600	500	1.20
4	80 : 20	580	490	1.18
5	70 : 30	580	500	1.16
6	60 : 40	570	500	1.14
7	50 : 50	570	510	1.12
8	30 : 70	550	490	1.12
9	20 : 80	530	475	1.12

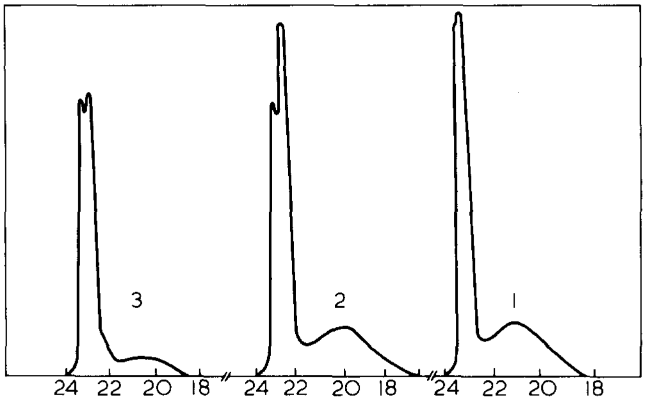

Figure 1 Gel chromatograms of byproducts of *p*-benzoquinone-styrene copolymerization in the presence of BF_3OEt_2 (for conditions see *Table 2*)

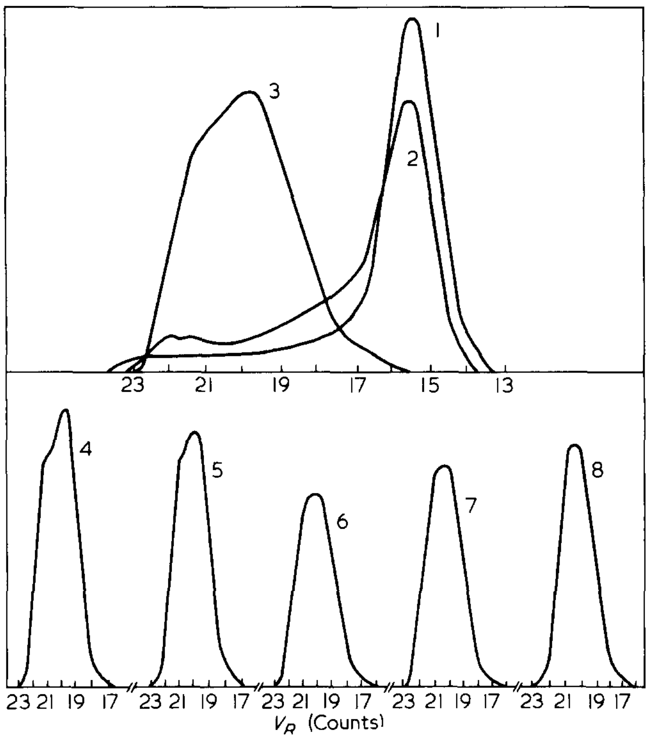

Figure 2 Gel chromatograms of polystyrene (1) and *p*-benzoquinone–styrene copolymers obtained in the presence of $BF_3 \cdot OEt_2$ (for copolymerization conditions see *Table 1*). BQ in mol l^{-1}: 0(1); 2(2); 10(3); 20(4); 30(5); 40(6); 50(7); 60(8)

Table 2 Composition of byproducts of copolymerization and *MWD* of oligohydroquinone. St : BQ = 50 : 50 mole %; $[St]_0 + [BQ]_0 = 0.70$ mol l^{-1} $T = 20°C$

No	Synthesis conditions $[BF_3 \cdot OEt_2]_0$, mol l^{-1}	Time, (h)	Content (wt. %) Quinhydrone	Hydroquinone	Polyhydroquinone	*MWD* (from g.p.c.) $\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_w/\bar{M}_n$ Calculated
1	0.0047	60	54.89	31.16	13.95	730	650	1.12	1.16
2	0.0063	60	51.01	37.46	11.53	690	620	1.11	1.17
3	0.0080	60	39.01	52.94	8.05	490	460	1.06	1.22

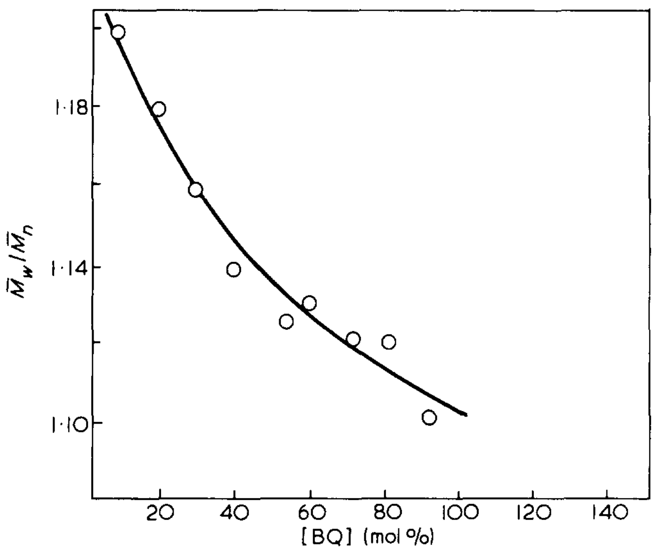

Figure 3 Polydispersity of *p*-benzoquinone–styrene copolymers vs. mole fraction of quinone in the reaction mixture

predominated in the BQ–St copolymer as is evident from the *MWD* curves of copolymers; the maxima of the curves are situated at 19.25 to 20.0 on the *X*-axis of the graph. These values define the retention volume (V_R).

DISCUSSION

The dependence of molecular weights and *MWD* of copolymers on the conditions of cationic copolymerization indicates the determining role of BQ on characteristics. In particular, cationic polymerization of styrene in the presence of small amounts (2 mole%) of BQ leads to the sharp variation in general picture of the *MWD* curves (see *Figure 2*). One can observe the displacement of the maximum on these curves to the lower molecular weights and decrease of $\bar{M}_n$ and $\bar{M}_w$ values from 1910 and 6700 to 1460 and 3370 respectively. The most important point in these variations, evidently, is a sharp decrease in the polydispersity coefficient from 3.51 to 2.31.

Increase of BQ to 10 mole% in the reaction mixture leads to decrease in $\bar{M}_w/\bar{M}_n$ for the copolymers to 1.20 and $\bar{M}_n$ and $\bar{M}_w$ to 500 and 600 respectively. A further increase of the BQ fraction to 90 mole% leads to an insignificant decrease of these characteristics (see *Figure 3*) and to narrowing the *MWD* curves.

The comparison of the theoretical Poisson distribution with polydispersity values found experimentally points to the rather narrow *MWD* of copolymers. The similar conclusion follows from *Figure 4* which shows the functions of *MWD* for five copolymers although they differ in width of the *MWD*.

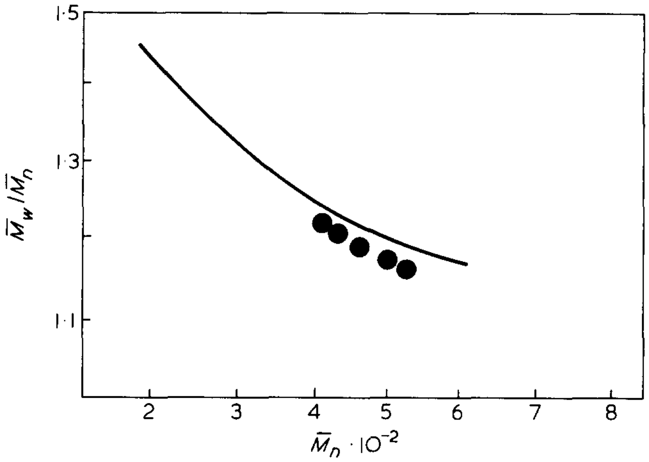

Figure 4 Comparison between $\bar{M}_w/\bar{M}_n$ values found experimentally (points) and Poisson's *MWD* (solid line)

The *MWD* curves (*Figure 2*) for copolymer synthesized in the presence of BQ (40–90 mole%) have a monomodal character. However those for copolymer obtained with 10–30 mole% of BQ at $V_R = 21–22$ exhibited a shoulder. It is obviously the low content of BQ that leads to the formation of St homopolymer[3] along with copolymer.

Thus, g.p.c. analysis of the products allows us to conclude that in this process BQ is a copolymer macromolecule regulator. This together with high yields of copolymers may be explained by BQ participation in chain transfer.

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