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Dilatometric Study of the Kinetics of the Polymerization of Pure meta- and Pure para-Divinylbenzenes

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SUMMARY

A comparison of the dilatometrically determined rates of polymerization of pure meta- and pure para-divinylbenzenes confirms the previous observation that the meta isomer polymerizes more rapidly than the para isomer. This difference shows up also in the initiator square root rate dependencies, the gel times, and the conversions at gel point. The effect of added regulator (carbon tetrabromide) on the polymerization of the meta isomer is to decrease the gel time and conversion at gel time.

INTRODUCTION

In previous studies [1] we have shown that it is possible to obtain viscometric data for the kinetics of the pregelation period in the polymerization of m- and p-divinylbenzene. The data show overall rate differences for the isomers and establish the desirability of having further data available from which some understanding of the details of the polymerization kinetics of divinyl monomers can be derived.

EXPERIMENTAL

Materials

The m-divinylbenzene was obtained as a 95% pure sample from Labofina, Brussels, and was purified by preparative gas chromatography as previously described [3]. The sample used was 99.9% pure by gas chromatographic analysis with flame ionization detector. p-Divinylbenzene was purified by preparative gas chromatography as previously described [2]. The sample used in the present work was 99.9% pure by gas chromatographic analysis with flame ionization detector. The monomers were distilled over a pellet of potassium hydroxide and collected in a cold receiver just before use. The benzoyl peroxide was reprecipitated from chloroform solution with methanol and dried under vacuum at room temperature. The toluene was boiled over sodium for 10 hr and redistilled before use. Carbon tetrabromide was recrystallized from methanol-water; mp, 90.1°C.

Polymerization Rate Determination

These rates were followed dilatometrically with a dilatometer of standard design [4-6] as described in detail by Schulz [6]. The monomer initiator and solvent were charged into the reaction tube of the dilatometer in the total amounts stated in Table 1. Unless other wise specified, all experiments were made at a concentration of 2.28 moles of monomer per liter of toluene. The reaction tube (about 3-ml capacity) was mounted in an evacuation chamber into which the graduated capillary tube (o.d., 0.5 mm; length, 60 cm) was inserted through an adapter sealed with a rubber tube. The whole chamber was flushed with prepurified nitrogen and degassed under vacuum. The ground-glass joint of the graduated capillary was then inserted into the joint on the reaction tube so as to force reactants into the capillary. After removal from the chamber, the closed joint of the reaction tube and capillary tube was sealed with mercury. The dilatometer was placed in a bath held at 70.0 ± 0.01°C. Time and volume contraction were measured at 1-min intervals from the moment of insertion in the bath. The observed data are recorded in the accompanying figures and tables.

Gel-Point Determination

The monomer (about 1.5 ml) with initiator was placed in the reaction tube (o.d., 1.5 cm; length, 10 cm), which contained a small, Teflon-coated,

Table 1. Kinetic Data for the Dilatometric Polymerization of Pure meta- and Pure para-Divinylbenzenes in Toluene at 2.28 Moles/Liter

Initiator concentration, moles/liter X 10^{-3}	Rate, (%/min) X 10		Gel time, min		Conversion at gel time, %	
	meta	para	meta	para	meta	para
0.82	0.63		286		17.10	
0.86		0.39		359.5		14.52
1.22	0.77		238		17.92	
3.10	1.40	0.83	130	180.2	18.37	16.55
3.11				190.2		14.50
7.29	2.12	1.44	91	126.5	18.67	16.23
12.10				91.8		17.80
12.20	3.20		64		19.75	
18.28	3.70		57		19.64	
18.31		2.30		76.2		16.92
30.15	4.47		46		21.83	
30.56		2.92		65.2		19.70
81.40			33.5		25.63	
81.51				54.8		22.50

magnetic stirrer (o.d., 0.3 cm; length, 1.2 cm). The monomer was degassed in three freeze-thaw cycles under vacuum. The tube was flushed with pre-purified nitrogen and sealed under vacuum. The tube was immersed in a bath at 70.0 ± 0.01°C, and the magnetic stirrer was placed in rotation. The gel time was taken as the time interval between immersion of the sample in the bath and the time at which the magnetic stirrer ceased rotation. Exploratory experiments indicated that the stirring ceases at the same gel time as that observed dilatometrically. The data are summarized in the figures and tables.

Conversions at Gel Point

These were determined by immediately transferring the polymerization mixture at the time of gelation in the gel-point determination procedure to a centrifuge tube in which the insoluble polymer was precipitated by addition of one part of benzene (containing inhibitor) and then 10 parts of methanol. This washing process was repeated two more times. The solvent was decanted from the centrifuged polymer. The polymer was dried under vacuum at

Table 2. The Effect of a Regulator on the Polymerization of m-DVB in Toluene Solution at 70°C[a]

$[R]\ 10^2$,[b] moles/liter	Gel time, min	Conversion at gel time, %
0.04	44.5	24.10
0.50	57.2	–
1.27	71.5	25.69
1.26	70.2	26.43
2.30	85.5	31.06
3.05	97.6	32.86
3.90	108.6	35.57
4.69	119.2	37.26
5.33	125.8	37.26
5.94	132.0	38.91

[a] Monomer concentration, 2.28 moles/liter; benzoyl peroxide concentration, 0.0362 mole/liter.

[b] [R] = regulator (carbon tetrabromide) concentration.

50°C to constant weight. The observed data are summarized in the figures and tables.

RESULTS

The conversion data (Fig. 1) for m-DVB show that the conversion is directly proportional to the polymerization time at intervals up to the gel time at about 90 min and 19.3% conversion, at which time the conversion sharply increases. Comparable data for the para isomer also show the conversion to be proportional to the polymerization time up to gelation at 126 min and with a conversion of 16% at gelation. Experiments with varying initiator concentration show (Fig. 2) that the polymerization rates in per cent conversion per minute are directly proportional to the square root of the initiator concentration over a range of initiator concentrations of 0.00082-0.081 moles/liter. The meta isomer polymerizes more rapidly than does the para isomer over

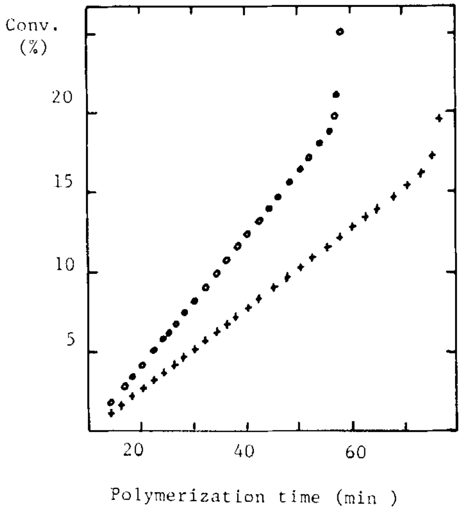

Fig. 1. Polymerization of m- (O) and p- (+) divinylbenzenes in toluene at 70°C. Concentration of DVB, 2.28 moles/liter; of dibenzoyl peroxide, 7.29 X 10^{-3} moles/liter. Conversion vs. time. Dilatometric data.

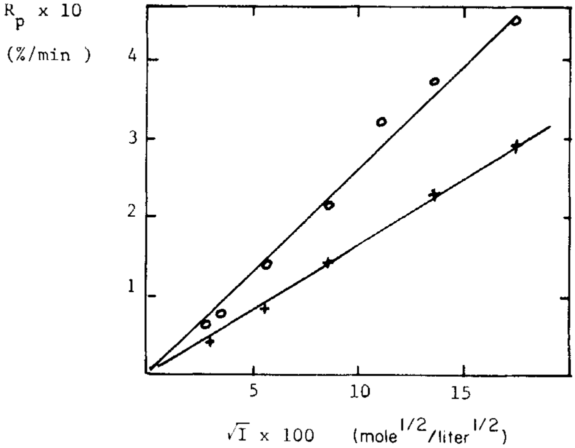

Fig. 2. Polymerization rates, R_p, in per cent per minute vs. square root of initiator concentration for the polymerization of m- (O) and p- (+) divinylbenzenes in toluene at 70°C.

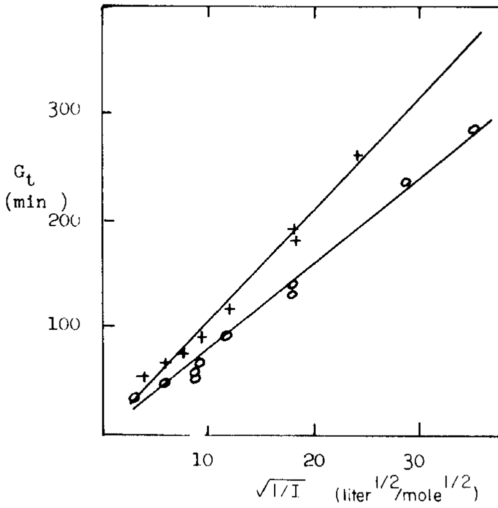

Fig. 3. Gel time (min) vs. reciprocal of the square root of the initiator concentration for the polymerization of m- (O) and p- (+) divinylbenzenes in toluene at 70°C.

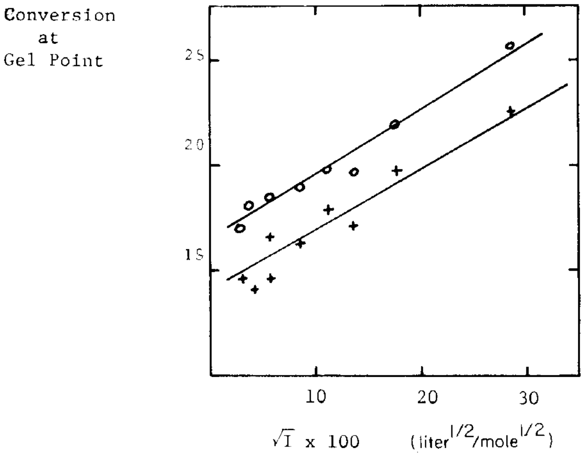

Fig. 4. Conversion at gel point vs. square root of the initiator concentration for the polymerization of m- (O) and p- (+) divinylbenzenes in toluene at 70°C.

this entire range. The gel time is linearly related (Fig. 3) to the reciprocal of the square root of the initiator concentration for both isomers, and there is a consistent difference between the isomers, with the lower gel times for the meta isomer. The relation between conversion at gel time and the square root of the initiator concentration (Fig. 4) also shows a difference in the behavior of the two isomers. The conversion at gel point for the para isomer is consistently lower than that for the meta isomer.

The data for the polymerization of m-DVB in the presence of carbon tetrabromide as regulator, at constant monomer and initiator concentration and varying regulator concentration, show that the gel time and per cent conversion at gel point are both proportional to regulator concentration over the range of regulator concentration of 0.004-0.0594 mole/liter. The gel time is longer and conversion at gel point is lower in the presence of the regulator.

DISCUSSION

It is apparent from the data now available that up to the gel point the kinetics of the polymerization of divinyl monomers have the characteristics shown by typical monovinyl monomers. The rate is linear, dependent on the square root of the initiator concentration, and subject to the usual regulator effects in the pregelation range. This is consistent with the generally accepted concept that the second vinyl group of the divinyl monomer is not involved prior to gelation. The second vinyl group appears to function, at least in the divinylbenzenes, as a substituent which modifies the reactivity of the reacting vinyl group.

The gelation characteristics of the divinylbenzene isomers show distinctions which appear to be related to different cross-linking processes. Thus, although gelation time appears to be a function of rate, i.e., the lower the rate the longer the time to gelation, and thus also to be a function of polymer concentration buildup, this cannot be the only factor involved because the conversion at gelation also varies for the two isomers. If everything were strictly comparable the conversion at gelation should be equivalent. The data at hand show this not to be so. At every rate level the more slowly polymerizing para isomer shows a lower conversion at gelation. This requires that less monomer be incorporated in the cross-linked para structure at gelation and suggests that there is greater molecular weight buildup prior to cross-linking in the meta-derived polymer. It may also be that the para-derived polymer, because it is structurally different, is simply less soluble than the meta-derived polymer.

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