

Bulk Polymerization of Diallyl Benzene-Dicarboxylates. II. Effect of Temperature on the Gel Point

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Synopsis

The effect of bulk polymerization temperature on the gelation of diallyl phthalate (DAP), diallyl isophthalate (DAI), and diallyl terephthalate (DAT) has been investigated in the temperature range 353–568 K (80–295°C). The critical double-bond conversion at the gel point increases significantly with temperature in a different manner for each of the monomers: for DAP, from ca. 17% at 353 K up to 46% at 568 K, whereas for DAI and DAT, from 15% and 13.5% up to 32 and 33%, respectively. These values are, on average, four to six times higher than those predicted according to Stockmayer's equation. Surprisingly, the yield of prepolymer precipitated just before the gel point is almost the same for DAP, DAI, and DAT at every polymerization temperature despite different tendencies to cyclization for each of the monomers. The yield increases significantly with the temperature: from ca. 24% at 353 K up to above 60% at 568 K. These yields are four to six times higher than are critical prepolymer contents predicted according to Gordon's theory. Empirical relationships between the gel point parameters and temperature have been developed.

INTRODUCTION

In our previous paper on the bulk polymerization of diallyl benzene-dicarboxylates,¹ the influence of temperature on the reactivity of the allyl groups of diallyl phthalate, isophthalate, and terephthalate (DAP, DAI, and DAT, respectively) was discussed. Despite their almost identical physicochemical properties, these isomers show distinct differences in the allyl group reactivities. For instance, in the early stages of the process, the rates of allyl group polymerization were distinctly different. On the other hand, polymerization of such a polyfunctional system is characterized by the gel point at which the system's viscosity increases rapidly with the ultimate loss of solubility. Thus, the gel point problem becomes extremely important in the polymerization of these compounds in practice.

The influence of temperature on the gel point in the polymerization of isomeric diallyl benzene-dicarboxylates has not been reported so far. In spite of the work of Gordon,² Simpson et al.,^{3,4} and Matsumoto et al.,⁵ it is also not clear to what extent the gel point depends on the structure of diallyl monomers.

The main purpose of the present work is to elucidate the influence of temperature on the gel point in bulk polymerization of isomeric diallyl benzene-dicarboxylates.

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EXPERIMENTAL

Materials and Polymerization Procedure

Monomers and initiators were prepared, and polymerization and precipitation of polymers were achieved by methods described previously.¹ To diminish the effect of chain transfer to initiator, the smallest possible amount of initiator was used. Thus, AIBN was used at the minimum concentration that would generate the gel point at 353 K. In the temperature range 430–500 K, the polymerization was initiated by the very small concentration (0.0025 mol/L) of cumene hydroperoxide, and at higher temperatures, polymerization was initiated thermally.

Polymerization was carried out under nitrogen in a three-necked flask equipped with an agitator. A fluidity loss of the polymerization mixture was observed at the gel point, causing the mixture to form one lump attached to the impeller. Solubility in chloroform was checked parallelly, and it was found that at the fluidity loss point solubility was also lost. The gel point was sharp and reproducible.

Analyses of Polymers

The number-average molecular weights were determined by membraneless osmometry at 37°C in chloroform using a Hewlett-Packard vapor pressure osmometer. The iodine numbers were determined by the Wijs method. The degree of unsaturation (U) was expressed as the ratio of the iodine number of polymer to that of the monomer.

The structure of polymers was investigated by the procedure of Simpson et al.⁴ Thus, saponification with potassium hydroxide was effected by refluxing under nitrogen a weighed portion (ca. 10 g) of polymer for 24 h with an adequate amount of 0.5 N alcoholic KOH (3 moles of base per 1 mole of ester groups). Titration of samples after 20 and 24 h indicated that saponification was complete. Linear chains of poly (allyl alcohol) were produced by hydrolysis of the ester groups in poly (diallyl esters). The alcoholic solution of poly (allyl alcohol) was then filtered using a Büchner funnel with a fritted disc. Following filtration, solid carbon dioxide was added slowly until precipitation was completed. The solution was filtered again, and the solvent was removed by distillation under nitrogen. Then, 10 mol of acetic anhydride per 1 mol of alcoholic groups was added and refluxed for 10 h under nitrogen. Excess acetic anhydride was subsequently removed under reduced nitrogen pressure. The resultant polymer was then taken up in benzene, washed repeatedly with water, and dried over anhydrous sodium sulphate. The poly (allyl acetate) was finally isolated by distillation under reduced nitrogen pressure and dried under vacuum at 25°C.

RESULTS AND DISCUSSION

It is known that diallyl prepolymer-monomer mixtures can be used for impregnating materials such as glass cloth to obtain heat-resistant wall panel and furniture finishes.⁶ The preferred way to obtain this mixture is polymerizing the diallyl monomer without precipitation of the prepolymer. In these appli-

cations, it is important to achieve as high a conversion of the double bonds as possible without gelling the mixture, since a high double-bond conversion in the prepolymerization process results in lower shrinkage during molding and curing steps.

To determine the critical double-bond conversion value at the gel point, the bulk polymerization of diallyl phthalates was carried out at various temperatures up to the gel point, and the progress of polymerization was followed by determining the residual double-bond concentration by the Wijs method. Determination of the conversion by this method can be carried out only on a fully soluble system. Therefore, the critical double-bond conversion value at the gel point was found by extrapolating the conversion-time data to the time at which the fluidity and solubility of the reaction mixture was lost by gelation. Such an extrapolation is justified because measurements of the refractive index of the polymerization mixture before and at the gel point showed no abrupt change at the onset of gelation. Figure 1 shows the dependence of the critical double-bond conversion value at the gel point on the polymerization temperature for DAP (curve 1), DAI (curve 2), and DAT (curve 3). It is seen that for each of

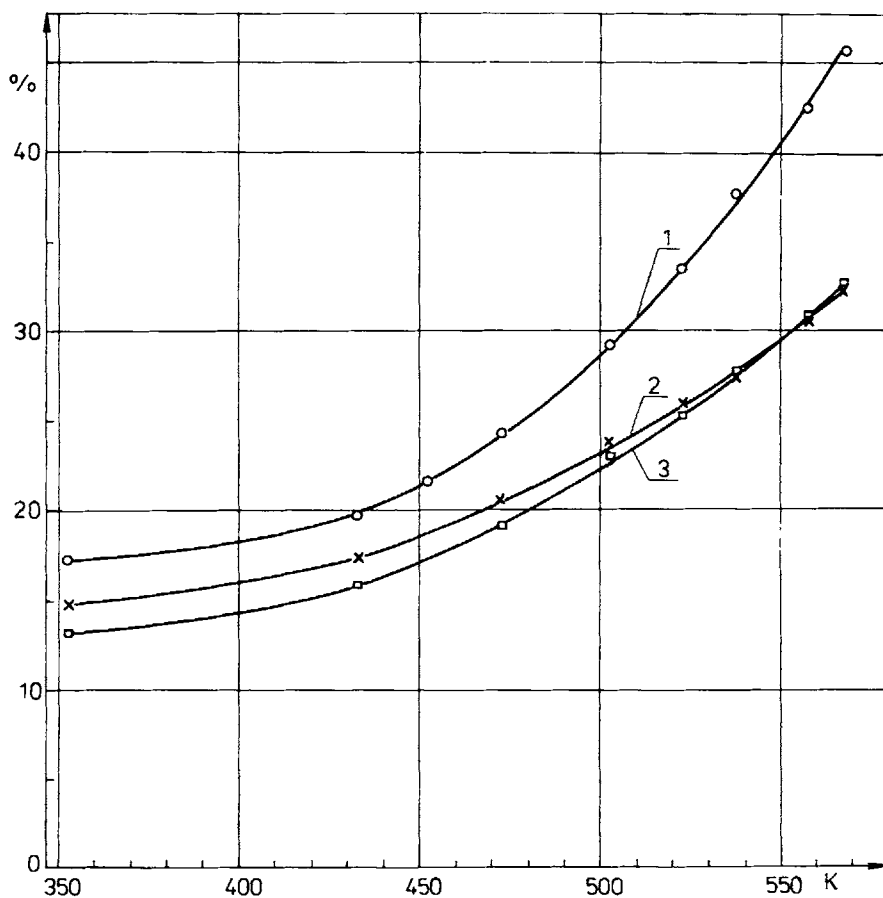


Fig. 1. Influence of temperature, T , on the critical double-bond conversion at the gel point, α_c , during the bulk polymerization of (1) (-O-O-) DAP, (2) (-x-x-) DAI, and (3) (-□-□-) DAT.

the monomers examined this critical double-bond conversion value increases significantly with temperature. However, the temperature dependence differs for each monomer. Thus, for DAP, the critical conversion value increases from ca. 17% at 353 K (80°C) to more than 40% at temperatures above 550 K, whereas for DAI and DAT, the critical conversion value increases from 15% and 13.5% to above 30%, respectively. This means that the polymerization temperature can increase the critical conversion value by a factor of 2 to 2.5.

This relationship between the critical double-bond conversion value and the temperature in the range 353 to 568 K can be described by the following empirical equations with the parameters estimated through a least-squares algorithm:

$$\alpha_{c,\text{DAP}} = 1.073 \exp 0.01607(T - 353) + 16.14, \quad r = .997 \quad (1)$$

$$\alpha_{c,\text{DAI}} = 1.122 \exp 0.01383(T - 353) + 13.63, \quad r = .995 \quad (2)$$

$$\alpha_{c,\text{DAT}} = 1.086 \exp 0.01428(T - 353) + 12.44, \quad r = .999 \quad (3)$$

where α_c is the critical double-bond conversion in %; T , absolute temperature; and r , correlation coefficient.

It is interesting to determine to what extent the results obtained could be predicted theoretically on the basis of the system's initial parameters. As seen in Figure 1, the ordering of critical conversion values of the isomeric diallyl benzene dicarboxylates is found to be *ortho* > *meta* > *para*. This suggests that the critical conversion value may increase with the increasing probability of cyclization within monomer units. If cyclization occurs, the monomer unit incorporates both of its double bonds into the same polymer chain, i.e., it behaves like two molecules of the monoallyl compound. On the other hand, when diallyl monomer units are polymerized normally, they have only one double bond reacted and form "pendant" double bonds. These pendant allyl groups are responsible for crosslinking.

This situation is similar to that considered theoretically by Flory, and by Stockmayer.⁷ It is well known that Flory developed a general equation relating the critical conversion at gelation (α_c) to the weight-average functionality (f_w) of the initial system for the case of polycondensation reactions

$$\alpha_c = 1/(f_w - 1) \quad (4)$$

In the particular case of a vulcanization reaction, where the initial polyfunctional material consists of chains of units bearing a single functionality (crosslinking position), f_w is simply the weight-average degree of polymerization (P_w) of the initial material. Thus,

$$\alpha_c = 1/(P_w - 1) \quad (5)$$

Equation (5) was extended to the special case of polymerization of symmetrical divinyl monomers by Stockmayer. He obtained an expression for predicting the gel point in addition copolymerization of monovinyl and divinyl

monomers. In this expression, it was assumed that the structure of both monomers is so closely related that all double bonds have the same reactivity, and

$$\alpha_c = 1/\rho(P_w - 1), \quad (6)$$

where P_w is the weight-average degree of polymerization of the linear chains that would result if all the crosslinks were broken and ρ is the fraction of all the double bonds residing on divinyl units in the initial system.

Simpson et al.⁴ applied the above equation to polymerization of DAP at 80°C. Assuming monodispersity of linear C—C chains obtained by hydrolysis of the branched poly (diallyl phthalate) macromolecules, they calculated the critical double-bond conversion to be 13.5%. Experimentally, they determined the conversion to be 18.5%.

We wanted to check the agreement between the calculated and determined critical conversions at different temperatures for DAP, DAI, and DAT. Therefore, we calculated the critical conversion according to Stockmayer's eq. (6) for all the isomers at selected temperatures (353, 433, 503, and 558 K, i.e., 80, 160, 230, and 285°C). Prepolymers were precipitated at the initial stage of polymerization when the probability of crosslinking is very small. Unsaturation of each of the prepolymers, expressed as a fraction of that for the monomer, was determined. If the unsaturation equals U , it means that the fraction ρ of all initial double bonds residing on diallyl monomer units that reacted normally, i.e., they formed pendant double bonds, equals $2U$.

Linear C—C chains were recovered by hydrolysis of the prepolymer, and number-average numbers of reacted allyl groups per chain were determined. In our previous paper,¹ it was shown that in the bulk polymerization of diallyl benzene-dicarboxylates an effective chain transfer to the allyl group is of great importance. This means that one could treat this polymerization as a process in the presence of a chain transfer agent. Thus, it can be assumed that the weight-average number of reacted allyl units per chain is twice the number-average value. Taking this into account, we calculated the critical conversion according to Stockmayer's eq. (6) and compared it to the measured values. Table I summarizes the results. It can be seen that the critical conversion values determined experimentally are much higher than those calculated according to Stockmayer. It means that the discrepancy between predicted and actual critical double-bond conversion observed by Simpson was not fortuitous. It also means that in practical applications the critical double-bond conversion in the polymerization of diallyl dicarboxylates is difficult to predict accurately on the basis of Flory-Stockmayer's theory.

One can also consider the gel point of diallyl phthalates from the viewpoint of the prepolymer content. When the polymerization of these monomers is applied to prepolymer production, it is obviously important to obtain as high a yield of the prepolymer as possible. The highest prepolymer content in the polymerization mixture occurs just before the gel point.⁶ In the next series of polymerizations, we precipitated the prepolymer just before the gel point, when the system was still soluble. We investigated the influence of polymerization temperature on the prepolymer yield for all three isomeric diallyl

TABLE I
Critical Double-bond Conversion α_c Calculated According to Stockmayer's Eq. (6)
in Comparison with Measured Values^a

Temperature [K (°C)]	Monomer	ρ	P_w	α_c (%)		
				Calcd	Measd	Measd/Calcd
353 (80)	DAP	0.606	54.4	3.1	17.2	5.5
	DAI	0.832	50.2	2.4	14.9	6.2
	DAT	0.926	51.6	2.1	13.6	6.5
433 (160)	DAP	0.590	46.6	3.7	19.8	5.4
	DAI	0.856	37.0	3.2	17.3	5.4
	DAT	0.978	38.0	2.8	16.1	5.7
503 (230)	DAP	0.656	26.0	6.1	29.4	4.8
	DAI	0.938	23.4	4.8	23.8	5.0
	DAT	1.038	19.4	5.2	23.3	4.5
558 (285)	DAP	0.740	14.8	9.8	42.7	4.4
	DAI	1.040	16.8	6.1	30.7	5.0
	DAT	1.138	12.8	7.4	31.2	4.2

^a $\rho = 2U$, where U is unsaturation of the prepolymer expressed as a fraction of that for the monomer; $P_w = 2P'$, where P' is the number-average number of reacted allyl groups.

benzene-dicarboxylates. The results are shown in Figure 2. It is interesting that in spite of different critical double-bond conversion values (see Fig. 1), DAP, DAI, and DAT exhibit similar values of the maximum prepolymer yield. This is observed over the entire wide polymerization temperature range studied. It is noteworthy that these prepolymer yields increase significantly with the temperature: from ca. 24% at 353 K (80°C) up to above 60% at 568 K (295°C).

The dependence of the yield (Y) of prepolymer on the absolute temperature (T) can be described by the following empirical equations, obtained by the least-squares procedure:

$$Y_{\text{DAP}} = 23.1 + \exp 0.01680(T - 353); \quad r = .995 \quad (7)$$

$$Y_{\text{DAI}} = 23.6 + \exp 0.01656(T - 353); \quad r = .995 \quad (8)$$

$$Y_{\text{DAT}} = 23.4 + \exp 0.01702(T - 353); \quad r = .994 \quad (9)$$

On the other hand, it would be useful to predict the highest prepolymer yield for a given monomer and temperature on the basis of initial parameters of the system. This aspect was previously investigated by Gordon,² Simpson and Holt,³ and Matsumoto et al.⁵

Gordon² predicted that the critical prepolymer content for a polymerizing monomer, which can undergo cyclization, is given by

$$(1 - b_c) = 1 - [R(2P_w - 3) - 1]^2 / [R(2P_w - 3) + 1]^2 \quad (10)$$

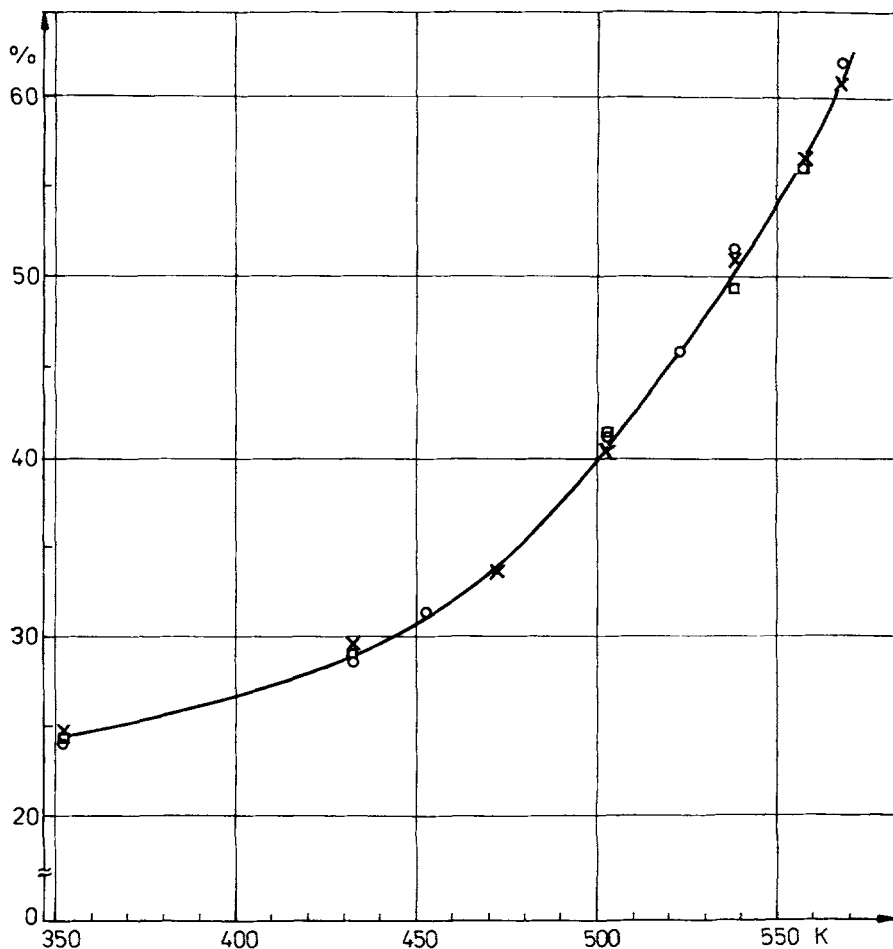


Fig. 2. Influence of temperature, T , on the yield of prepolymer just before the gel point, Y , in the bulk polymerization of (○) DAP, (×) DAI, and (□) DAT.

where $(1 - b_c)$ is the prepolymer content at the gel point, R is the fraction of monomer units in the prepolymer that are found to have reacted normally (i.e., without cyclization), and P_w is the weight-average number of divinyl monomer units per single chain. Gordon applied the above equation to the polymerization of DAP and, assuming uniform chains ($P_w = P_n$), obtained a good correlation.

Simpson and Holt³ tried to check Gordon's equation against diallyl ester monomers other than DAP, including DAI, DAT, diallyl oxalate, and diallyl sebacate. In all cases, gelation at 80°C occurred at a conversion higher than the value predicted by eq. (10).

Subsequently, Matsumoto et al.⁵ reexamined experimentally the critical polymer content in the polymerization of DAP, DAI, and DAT at 80°C. They compared their results with those from Gordon's theory and found that the discrepancy between the actual and theoretical gel point was quite large.

On the basis of our results, we were able to check the validity of Gordon's equation over a very wide temperature range. We precipitated the prepolymer at the initial stages of polymerization and determined unsaturation, U , and number-average numbers of diallyl monomer units, P . Chain lengths in the bulk polymerization of these monomers are predominantly determined by chain transfer reactions.¹ Thus, one may assume that the weight-average number of diallyl monomer units per chain is twice the number-average number. This is consistent with Matsumoto's findings.⁵ Taking this into account, we applied Gordon's eq. (10) and calculated the critical prepolymer content for DAP, DAI, and DAT polymerization at 353, 433, 503, and 558 K (80, 160, 230, and 285°C). The results, together with the prepolymer yield values determined in this work, are summarized in Table II. The results tabulated in the last row indicate that in all cases the determined prepolymer yields are several times higher than are the theoretically calculated [eq. (10)] critical values.

It should be noted that cyclization has no practical influence on the critical prepolymer content in the polymerization of diallyl benzenedicarboxylates. Furthermore, despite different tendencies for cyclization for these *ortho*, *meta*, and *para* isomers, they gel at almost the same prepolymer content over the entire investigated temperature range.

The results obtained indicate that the practically important gel point in the polymerization of diallyl dicarboxylates is difficult to predict on the basis of the initial parameters of the system. On the other hand, the empirical relationships found in this work for the bulk polymerization of these monomers enable one to determine the critical double-bond conversion and the maximum prepolymer yield at any temperature in the very wide temperature range 535–568 K (80–295°C).

TABLE II
Critical Prepolymer Content ($1 - b_c$) Calculated According to Gordon's Eq. (10)
in Comparison with Prepolymer Yield Y^a

Temperature [K (°C)]	Monomer	P_w	R	$1 - b_c$ (%)	Y (%)	$Y/(1 - b_c)$
353 (80)	DAP	79.6	0.606	4.13	24.1	5.8
	DAI	49.6	0.832	4.88	24.6	5.0
	DAT	43.8	0.926	4.98	24.4	4.9
433 (160)	DAP	76.2	0.590	4.44	28.6	6.4
	DAI	30.8	0.856	7.67	29.5	3.9
	DAT	35.6	0.978	5.82	29.0	5.0
503 (230)	DAP	43.0	0.656	7.08	41.1	5.8
	DAI	25.2	0.938	8.09	40.0	4.0
	DAT	18.6	1.038	10.66	41.6	3.9
558 (285)	DAP	25.2	0.740	10.78	56.2	5.2
	DAI	14.8	1.040	13.47	56.8	4.2
	DAT	13.2	1.138	13.95	56.1	4.0

^a $P_w = 2P$, where P is the number-average number of diallyl monomer units per chain obtained at initial stages of polymerization; $R = 2U$, where U is unsaturation of the prepolymer expressed as a fraction of that for the monomer.

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