

Polymerization of Diallyl Phthalate at High Temperatures

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Synopsis

The influence of high temperature (160–250°C) on diallyl phthalate polymerization has been investigated. Polymerization was carried out in a nitrogen atmosphere both with and without benzoyl peroxide as initiator, and also in a air atmosphere. A considerable increase in the conversion degree to the gelation point with a parallel increase in temperature has been established. Unsaturation degree of prepolymers remains unchanged independently of temperature and the way of polymerization initiation.

INTRODUCTION

Polymerization of diallyl esters can be successfully carried out at high temperatures. Mednick¹ polymerized diallylic phthalate monomers by heating at temperatures of under 225°C in the presence of a free radical initiator the effect of which is sharply reduced within a few minutes and completing the polymerization by heating alone. An alternative way is to polymerize diallylic phthalate monomers either at 200°C or above in an inert atmosphere thermally without initiator or by using an initiator in such small quantities that it is substantially destroyed before the end of the polymerization process.²

As has been found in preliminary tests, polymerization of diallyl esters of phthalic acid at high temperatures seems to be interesting because high temperatures increase the reaction degree to the gelation point. Diallyl phthalate polymerization at 160–250°C was undertaken. The aim of the investigations was to explain the influence of the temperature on polymerization rate, monomer conversion degree to the gelation point, and prepolymer properties.

EXPERIMENTAL

Materials

As monomer, diallyl esters of *o*-phthalic acid were used. Before use, the monomer was purified by twofold vacuum distillation in a nitrogen atmosphere. The purified monomer was colorless, its refractive index was $n_D^{20} = 1.5198$, and iodine number was 206.7.

The initiator was benzoyl peroxide (BPO) purified by twofold precipitation with methanol from chloroform.

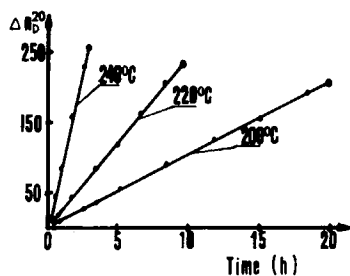


Fig. 1. Diallyl phthalate polymerization in nitrogen without initiator. Changes in refractive index of reaction mixture depending on time of different temperatures.

Polymerization

The prepolymers were prepared by bulk polymerization. Diallyl phthalate polymerization was carried out in a typical glass apparatus equipped with thermometer, stirrer, and reflux condenser. Polymerization in nitrogen atmosphere was carried out in the same apparatus equipped additionally with a nitrogen feeding and sampling system. The polymerization course was followed by measuring the refractive index of reaction mixture. Part of the polymerization was carried out just before the gelation point and the prepolymer (i.e., pregelled polymer) was precipitated from methanol.

Prepolymer Characterization

The unsaturation degree of the prepolymers was characterized by iodine number, determined by the Wijs method using mercury acetate as catalyst. Results were expressed in iodine number, showing number of grams iodine absorbed by 100 g investigated compound.

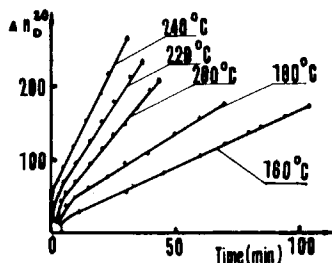


Fig. 2. Diallyl phthalate polymerization in air without initiator. Changes in refractive index of reaction mixture depending on time at different temperatures.

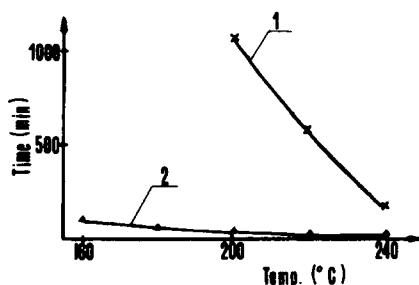


Fig. 3. Dependence of duration of polymerization to gelation on temperature without initiator in nitrogen (1) and air (2).

The softening temperature (T_s) of the prepolymers was determined by using a Boëthius apparatus at a rate of temperature increase equal to 5 deg/min.

Molecular weight (\bar{M}_n) of the prepolymers was determined by vapor osmometry using a Mechrolab 302 apparatus. Chloroform was used as solvent.

Molecular weight distribution was determined by gel chromatography using a Waters gel chromatograph model-200 with chloroform as a solvent.

RESULTS AND DISCUSSION

The polymerization course of diallyl phthalate was investigated by following the monomer conversion to the gelation point. The process rate evaluated on the basis of changes of refractive index of the reaction mixture during thermal polymerization in a nitrogen atmosphere (without initiator) was linear in the range of conversion up to the gelation point (Fig. 1).

A distinct two-stage process is observed when the reaction is carried out in an air atmosphere (Fig. 2). In the first stage, the process rate is relatively fast and becomes stabilized at a lower level in the second stage. The course of the above described polymerizations of diallyl phthalate in an air atmosphere suggests that oxygen takes part in the initiation. The higher rate of polymerization in air ensures that the duration of the thermal polymerization to the gelation point is considerable shorter than in the inert atmosphere (Fig. 3). This oxygen activity can be utilized in the initiation of diallyl phthalate polymerization at high temperatures. Thus, the polymerization rate can be regulated by controlled dosing of the air. An example of such a polymerization is shown in Figure 4.

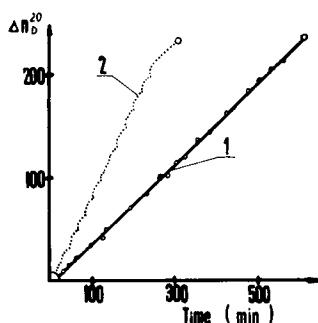


Fig. 4. Diallyl phthalate polymerization in nitrogen without initiator (1) and initiated by 5-ml air portions (2). Changes in refractive index of reaction mixture depending on time at different temperatures.

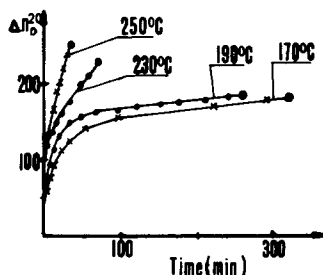


Fig. 5. Diallyl phthalate polymerization in nitrogen initiated by 0.01 mol/L BPO. Changes in refractive index of reaction mixture depending on time at different temperatures.

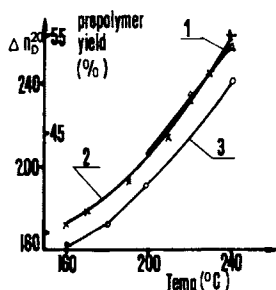


Fig. 6. Dependence of refractive index at gelation point and prepolymer yield on temperature for diallyl phthalate polymerization without initiator in nitrogen (1), in air (2), and in nitrogen with BPO 0.01 mol/L (3).

Diallyl phthalate polymerization initiated by the addition of a free radical initiator at such high temperatures proceeds violently and leads to rapid gelation. However, when proper small amounts of initiators are used, it is possible to obtain a controllable two-stage process. An example of such polymerization of diallyl phthalate initiated by BPO in the amount of 0.01 mol/L is shown in Figure 5. In such acute conditions, the initiator undergoes rapid decomposition and is entirely consumed during a very short reaction time leading to an apparent slowing down of the polymerization process. After the initiator has been consumed, the process becomes probably of thermal character. This is evident from the comparison of rates of the processes carried out on the inert atmosphere both in the absence and in the presence of an initiator. From the above observations, it can be stated that the degree of reaction to gelation is mostly influenced by temperature. The degree of reaction of the monomer to the gelation point estimated on the basis of refractive index is very similar for processes carried out both in inert and in air atmosphere (Fig. 6). Initiators cause a decrease in the degree of reaction at the gelation point, as noted in the previous investigations.³ The highest prepolymer (i.e., pregelled polymer) yield achieved in the experiments was 55%, thus increasing noticeably the efficiency of the process, in comparison with a 25% yield for the polymerization carried out at 80°C.

TABLE I
Properties of Investigated Diallyl Phthalate Prepolymers

Characteristics of polymerization	Iodine number	Softening temperature, °C	\bar{M}_n
Polymerization in nitrogen without initiator at:			
160°C	60	72-80	—
200°C	60	75-81	—
240°C	61	78-87	36.800
Polymerization in air without initiator at:			
160°C	59	72-80	—
200°C	59	70-79	—
240°C	61	70-78	30.800
Polymerization in nitrogen initiated by 0.01 mol/L BPO at:			
160°C	61	72-81	—
200°C	61	74-81	—
240°C	61	77-83	25.500



Fig. 7. Elution curves of diallyl phthalate prepolymers obtained at 250°C in N₂ atmosphere without initiator (1) and with 0.01 mol/L BPO.

Unsaturation degree and softening temperature of diallyl phthalate prepolymers obtained in the herein described experiments are very similar to each other independently of atmosphere and initiation was (Table I) and do not vary essentially from those of prepolymers obtained at lower temperatures. However, prepolymers synthesized at high temperatures are characterized by higher \bar{M}_n values (Table I).

Elution curves of all investigated samples of the prepolymers appear to have a characteristic shape indicating a wide molecular weight distribution and considerable content of polymeric products of very low molecular weight (Fig. 7). In the case of the prepolymer obtained with the initiator (BPO), a bigger maximum in the elution range $V_e = 30-35$ can be observed. That would indicate a slightly greater participation of low oligomers than in prepolymers obtained in thermal polymerization. Yet it should be pointed out that molecular weight distributions of prepolymers prepared at high temperatures are very similar to that of prepolymers obtained at 80°C.⁴ Despite the high temperature, the reaction mixture remained colorless, especially in nitrogen atmosphere. In the air and in the upper range of temperatures, a slight decomposition was revealed by yellowing and a strong odor. The prepolymer obtained in the experiments had the consistency of white friable powder.

References

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