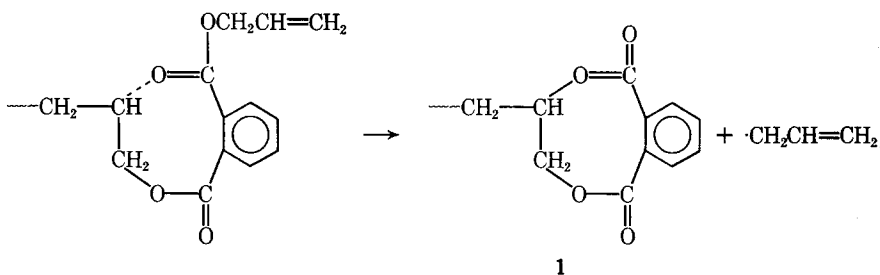


NOTES

Studies on the Diallyl Phthalate Prepolymers Capable of Initiating Polymerization at Elevated Temperatures. IV. Possibilities for Practical Application

INTRODUCTION

In our continuing studies of the radical polymerization of diallyl dicarboxylates,¹ we have attempted to investigate in detail the bulk polymerization of a variety of diallyl dicarboxylates at elevated temperatures by differential scanning calorimetry (DSC).² It has been found that the appearance of two exothermic peaks is rather characteristic of the polymerization of diallyl phthalate (DAP), although Kambe and Shibasaki³ have first observed for the curing of DAP resins previously gelatinized to some degree. In an attempt to elucidate this characteristic polymerization behavior of DAP, it has been suggested that the second peak is ascribed to the polymerization of unreacted monomer initiated by the DAP prepolymer (PDAP) obtained at the first exothermic temperature range.² Thereafter, this interesting initiation capability of PDAP's obtained under various polymerization conditions has been examined in detail;⁴ the highly active PDAPs are obtained under the following conditions: (1) polymerization temperature should be low such as at 30°C; (2) monomer concentration should be low; (3) polar solvent should be used; (4) polymerization time should be shortened, especially in the polymerization at a higher temperature. For example, the PDAP obtained in dioxane at 50°C using 2,4-dichlorobenzoyl peroxide showed 0.05 polymerization-initiation-activity of dicumyl peroxide. In our preceding article,⁵ we attempted to identify the unstable structural units in the PDAP capable of initiating the polymerization of DAP monomer at elevated temperatures; thus, by considering the following facts that (i) the initiation capability of PDAPs depends largely on their preparation conditions,⁴ (ii) poly(allyl propyl phthalate), the monomer of which corresponds to the monoene counterpart of the DAP monomer, shows a high polymerization-initiation-activity, and (iii) on the IR spectrum of the highly active PDAP, the characteristic absorption is clearly detected at 1760 cm⁻¹, the structural unit 1 introduced into the polymer chain end via the reaction shown below is presumed as being the initiation species of PDAP:



Thus, the present article is concerned with a brief discussion of the possibilities for practical application of PDAP capable of initiating polymerization at elevated temperatures.

EXPERIMENTAL

Materials. DAP and ethyleneglycol dimethacrylate (EGDMA), commercially available reagents, were distilled *in vacuo* under nitrogen before use. 2-Hydroxyethyl methacrylate (HEMA) was used as a commercially available special research grade reagent. Vinyl benzoate (VBz) was prepared from ester interchange of vinyl acetate with benzoic acid according to the method of Adelman⁶ and

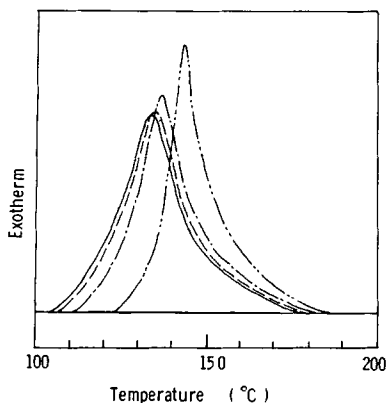


Fig. 1. DSC thermograms for the bulk polymerization of EGDMA in the presence of PDAP-3 (wt %) with heating rate of $10^{\circ}\text{C}/\text{min}$: (—) 9; (---) 5; (-·-) 1; (---) 0.

purified by vacuum distillation. Benzoyl peroxide (BPO) as an initiator and dioxane and benzene as solvents were purified by conventional methods.

Preparation of PDAP. DAP was polymerized as described previously.⁷ After a definite period of reaction time, the polymer produced was precipitated by pouring the reaction mixture into a large amount of chilled methanol. The polymer thus obtained was then washed several times with a small amount of methanol and dried *in vacuo* until a constant weight was obtained. The percentage conversion was calculated from the weight of the isolated polymer. The polymer was then purified by dissolving it in benzene and subsequently reprecipitating carefully with methanol to remove exclusively the low-molecular-weight polymer.

Polymerization Procedure by DSC. A Shimazu DT-30/SC-30 Differential Scanning Calorimeter was used. The NBS-ICTA standard reference materials 758 (KNO_3 , In, Sn, KClO_4 , Ag_2SO_4) were used as standards for thermal and calorimetric calibration. In each experiment a ca. 10-mg sample consisting of the corresponding monomer and PDAP was weighed out into an aluminum cell, which was then sealed. DSC measurements were carried out by the programmed heating rate of $10^{\circ}\text{C}/\text{min}$ from the room temperature to 250°C in a nitrogen atmosphere.

Estimation of Initiation Capability of PDAP. The initiation capability of PDAP was estimated by DSC. Thus, the amount of generated heat was calculated from the area under the exothermic DSC curve for the programmed heating polymerization of the reaction mixture of PDAP/DAP monomer (1/10 w/w) with heating rate of $10^{\circ}\text{C}/\text{min}$, and, then, the initiation capability H (cal/g)

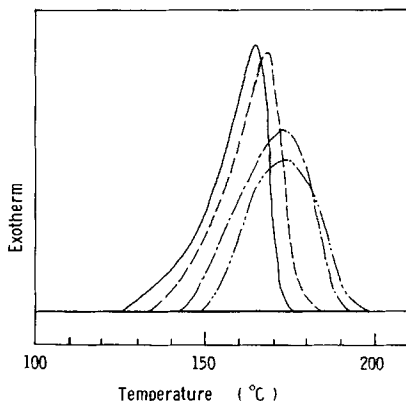


Fig. 2. DSC thermograms for the bulk polymerization of HEMA in the presence of PDAP-3 (wt %) with heating rate of $10^{\circ}\text{C}/\text{min}$: (—) 9; (---) 5; (-·-) 1; (---) 0.

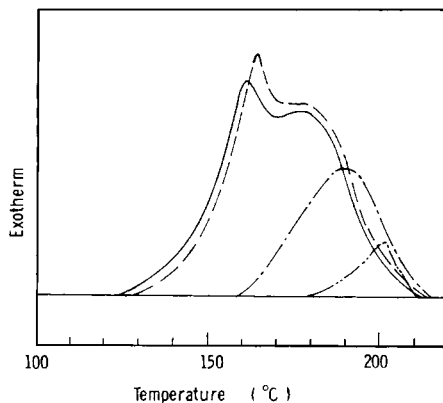


Fig. 3. DSC thermograms for the bulk polymerization of VBz in the presence of PDAP-3 (wt %) with heating rate of 10°C/min: (—) 9; (---) 5; (- - -) 1; (— — —) 0.

corresponding to the amount of generated heat per 1 g of the reaction mixture was estimated.

Curing. The PDAP/DAP monomer (1/1 w/w) mixture was poured into a silicone rubber container to a depth of a few millimeters and subjected to the heat treatment in an oven.

The cured product was pulverized, and, then, the unreacted monomer was extracted with methanol. The gel fraction of the cured product was separated by extracting the sol fraction with benzene.

RESULTS AND DISCUSSION

Self-Crosslinkability of PDAP. PDAP-1 was prepared and characterized as follows: DAP was polymerized in dioxane solution (DAP/dioxane = 1/4 v/v) using 0.05 mol/L of BPO at 80°C for 9 h; conversion, 60.3%; residual unsaturation R_{us} , 0.070; initiation capability H , 19.8 cal/g.

The self-crosslinkability of PDAP-1 was compared with that of commercially available PDAP-2 ($R_{us} = 0.285$, $H = 4.2$ cal/g). Thus, PDAP's were mixed with DAP monomer (PDAP/DAP monomer = 1/1 w/w) and cured at 185°C for 1 h; the gel and unreacted DAP monomer contents (%) of the cured products were 95.5 and 0 for PDAP-1 and 78.4 and 10 for PDAP-2, respectively. Self-crosslinkability of PDAP-1 having high initiation capability was considerably high compared to PDAP-2.

Here it should be noted that the content of the unreacted pendant allyl groups of PDAP-1 is quite low as opposed to the high value of PDAP-2. Clearly, PDAP-1 initiated effectively the polymerization of DAP monomer with the applicability for self-crosslinkable allyl resins; PDAP having appropriate amount of unreacted pendant allyl groups and appropriate initiation capability may be usefully chosen for practical application.

Polymerization of Some Vinyl Monomers Using PDAP as Initiator. PDAP-3 was prepared and characterized as follows: DAP was polymerized in benzene solution (DAP/benzene = 1/4 v/v) using 0.1 mol/L of BPO at 80°C for 8 h; conversion, 45.2%; initiation capability H , 18.5 cal/g.

PDAP-3 was then attempted to explore the usefulness as the initiator of vinyl monomers; EGDMA, HEMA, and VBz were polymerized in the presence of PDAP 3 without any usual radical initiator. Figures 1-3 show the DSC curves for the programmed heating polymerization of EGDMA, HEMA, and VBz, respectively, with heating rate of 10°C/min. The temperatures of onset of the polymerizations of EGDMA and HEMA were obviously shifted toward a lower temperature side with increasing the added amount of PDAP-3, although EGDMA and HEMA were polymerized thermally even in the absence of PDAP-3. In the case of VBz the polymerization-initiation-activity of PDAP-3 was evidently shown as a reflection of a low thermal polymerizability of VBz. These results suggest the usefulness of PDAP as the initiator of vinyl monomers. Noteworthy, the possibility that a trace of BPO which may be contained in PDAP-3 as a contaminant initiates the polymerization of vinyl monomers can be dismissed since the temperatures of onset of polymerization are quite high as compared with the decomposition temperature of BPO and additionally; no change is observed by using repeatedly reprecipitated PDAP-3. Furthermore, the annealed PDAP-3 ($H = 0.8$ cal/g) obtained after the heat treatment at 180°C for 2 h showed almost no initiation capability for VBz

polymerization, although the reduction of the initiation capability of PDAP by annealing at 180°C has been already observed as the relationship between H and annealing time.²

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