

# Some unsymmetrical azo compounds as initiators in radical polymerization

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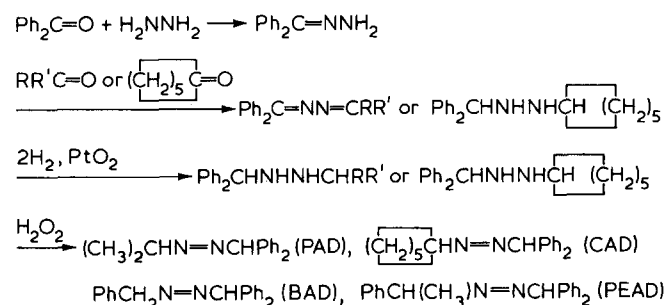
2-Propylazodiphenylmethane (PAD), cyclohexylazodiphenylmethane (CAD), benzylazodiphenylmethane (BAD) and 1-phenylethylazodiphenylmethane (PEAD) were prepared. These materials decomposed through first order reactions. The ease of decomposition increased in the order: CAD < PAD < BAD < PEAD, the rate being insensitive to the change in solvent. The rate constant of decomposition of PEAD was about twice that for 2,2'-azobisisobutyronitrile and that for CAD was nearly equal to that of benzoylperoxide. The initiation efficiencies were about 0.1 for CAD and PAD, 0.2 for BAD and 0.45 for PEAD. Transfer of polymer radical to the above unsymmetrical azo compounds was not negligibly small.

**Keywords** Decomposition; first order; radical polymerization; initiation efficiency; unsymmetrical azo; transfer

## INTRODUCTION

It is well known that azobisalkylnitriles initiate the polymerization of vinyl monomers. A typical azo compound is 2,2'-azobisisobutyronitrile (AIBN), which has been the most commonly used azo initiator. This decomposes effectively under conditions where the polymerization can be initiated, and its rate depends little on the kind of solvent<sup>1,2</sup>. However, *in vivo*, AIBN gives HCN, and heating the polymers prepared using AIBN also liberates HCN<sup>3</sup>. This shows that AIBN is toxic due, apparently, to cyano groups. Azo compounds which do not have cyano group have also been prepared by several workers<sup>4-8</sup>. The rates of decomposition of 1-azobis-1-phenylethane<sup>5</sup> and 1,1'-diphenylmethylazomethane<sup>7</sup> were so small that they could not be conveniently compared with that of AIBN. However, the rates of decomposition of azobisdiphenylmethane<sup>4</sup> and phenylazotriphenylmethane<sup>6</sup> were about twenty times greater than that of AIBN. The above facts show that these azo compounds, which do not have a cyano group, do not decompose at a convenient rate under the normal polymerization conditions. However, they also suggest that unsymmetrical azo compounds, having a diphenylmethyl group and an alkyl or a monophenylmethyl group, may decompose at a rate similar to that of AIBN.

In this report, 2-propylazodiphenylmethane (PAD), cyclohexylazodiphenylmethane (CAD), benzylazodiphenylmethane (BAD) and 1-phenylethylazodiphenylmethane (PEAD) were prepared by the following reaction process.



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where R is either H or CH<sub>3</sub> and R' is either CH<sub>3</sub> or Ph. The rates of their decompositions and their effectiveness as initiators in the polymerization of styrene are discussed and compared with those of AIBN and benzoylperoxide (BPO).

## EXPERIMENTAL

Benzophenone hydrazone was obtained from equimolar amounts of hydrazine hydrate and benzophenone by heating in ethanol under reflux<sup>4</sup>. Unsymmetrical ketone-azines were prepared by refluxing equimolar amounts of the benzophenone hydrazone and respective ketones (acetone, cyclohexane, benzaldehyde and acetophenone) in ethanol<sup>9</sup>. Unsymmetrical hydrazone was prepared by the hydrogenation of 0.1 mol ketone-azine in acetic acid (70 ml) in the presence of an Adams catalyst at a pressure slightly above atmospheric at room temperature. As was reported for the preparation of azobisdiphenylmethane<sup>5</sup>, it was convenient to remove the catalyst, neutralize the residual acetic acid with aqueous sodium bicarbonate, extract with ether, wash with water and boil off the ether. The oily product was oxidized in ethanol (70 ml) by a slight excess of 30% hydrogen peroxide for one day at room temperature. The resulting azo compounds were precipitated by adding water, extracted with ether, washed with water, dried over magnesium sulphate and concentrated. When the contaminants were removed by liquid chromatography, PEAD solidified (PEAD could be recrystallized from ethanol on standing at -25°C, without the chromatographic method). The other azo compounds were also purified by the chromatography. CAD and BAD solidified slowly, but PAD remained as an oil. The data are given in Table 1.

The rate constants of decomposition were measured as described previously<sup>1,2,4-8</sup>. Commercial styrene was purified and polymerized in the presence of the above unsymmetrical azo compounds, as described previously<sup>10</sup>. The conversion was below 10%. The chain length of the polymer was estimated from the intrinsic viscosity<sup>11</sup>.

## RESULTS AND DISCUSSION

The rate constant,  $k_d$ , of decomposition is shown in Table 2.  $k_d$  at 60°C increases in the order: PEAD > BAD > PAD > CAD. The  $k_d$  of PEAD is about

Table 1 Data on unsymmetrical azo compounds

Compound	Yield (%) <sup>*</sup>	M. pt. (°C)	Analysis (%)			N.m.r. (ppm <sup>**</sup> )				
			C	H	N	C <sub>6</sub> H <sub>5</sub>	Ph <sub>2</sub> CH	RR'CH	CH <sub>2</sub>	CH <sub>3</sub>
PAD	36	—	81.2 (80.7)	7.2 7.6	11.5 <sup>a</sup> 11.8 <sup>b</sup>	7.1–7.5 (10H)	5.72 (1H)	3.6–4.1 (1H)	—	1.2–1.35 (6H)
CAD	12	~25	81.6 (82.0)	8.2 7.9	10.2 <sup>a</sup> 9.6 <sup>b</sup>	7.1–7.5 (10H)	5.75 (1H)	4.0–4.5 (1H)	1.2–2.0 (10H)	—
BAD	60	~20	84.7 (84.0)	6.6 6.3	9.6 <sup>a</sup> 9.8 <sup>b</sup>	7.1–7.5 (10H)	5.76 (1H)	—	5.2 (10H)	—
PEAD	72	37	83.9 (84.0)	6.7 6.7	9.2 <sup>a</sup> 9.3 <sup>b</sup>	7.0–7.5 (15H)	5.76 (1H)	4.7–5.0 (1H)	—	1.52–1.60 (3H)

\* From the unsymmetrical hydrazine

\*\* TMS standard

<sup>a</sup> Found<sup>b</sup> Calculated

Table 2 Rate constants of decomposition of the unsymmetrical azo compounds

Compound	Temperature (°C)	Solvent	10 <sup>6</sup> k <sub>d</sub> (s <sup>-1</sup> )
PAD	60.0	Ethylbenzene	5.4
CAD	60.0	Ethylbenzene	3.8
BAD	60.0	Ethylbenzene	6.7
PEAD	50.0	Ethylbenzene	6.7
PEAD	60.0	Ethylbenzene	25.6
PEAD	65.0	Ethylbenzene	43.2
PEAD	80.0	Ethylbenzene	310
PEAD	80.0	Cyclohexanol	270
PEAD	80.0	Dimethylformamide	433
PEAD	99.0	Ethylbenzene	2500

twice that of AIBN<sup>2</sup>;  $k_d = 9.9 \times 10^{-6} \text{ s}^{-1}$  at 60°C. The  $k_d$  of CAD is nearly equal to  $k_{dBPO} = 2.76 \times 10^{-6} \text{ s}^{-1}$  in benzene<sup>12</sup>. The dielectric constants of dimethylformamide, cyclohexanol and ethylbenzene are 28.8, 9.39 and 2.26 at 80°C, respectively<sup>13</sup>. However, the effect of the dielectric constant is not clearly seen in the rate constant of PEAD. Thus, as in the symmetrical azo compounds<sup>1,2</sup>, the rate of the decomposition of the unsymmetrical azo compound is not affected appreciably by the change in solvent. Application of the Arrhenius equation to the data for PEAD gives:  $k_d = 2.0 \times 10^{14} \exp(-28800/RT)$  where  $R$  is a gas constant and  $T$  is absolute temperature.

The data of the bulk polymerization of styrene are treated by<sup>14</sup>:

$$\frac{[M]}{[C]} \left( \frac{1}{\bar{n}} - C_{trM} \right) = C_{tri} + f k_d \cdot \frac{[M]}{R_p} \quad (1)$$

where  $[M]$  and  $[C]$  are the concentrations of monomer and initiator, respectively;  $\bar{n}$  is chain length;  $f$  is the initiator efficiency;  $C_{trM}$  and  $C_{tri}$  are the relative transfer constants to monomer and initiator, respectively, where  $C_{trM} = 6.0 \times 10^{-5}$  is used<sup>14</sup> (Figure 1). From the intercepts of the lines,  $C_{tri}$  is estimated to be 0.04 (PAD), 0.04 (CAD), 0.07 (BAD) and about 0.1 (PEAD). These values are nearly equal to the transfer constant for BPO<sup>8,14</sup>. From the slopes and the  $k_d$  values in Table 2, the  $f$  values are calculated to be 0.10 (PAD), 0.12 (CAD), 0.20 (BAD) and 0.45 (PEAD). The  $f$  of PEAD is comparable with  $f \approx 0.5$  for AIBN and BPO<sup>14,15</sup>. However, the  $f$  values of PAD, CAD and BAD are considerably less than 0.5.

It is therefore concluded that PEAD is recognized as one of the better initiators, because the yield in its

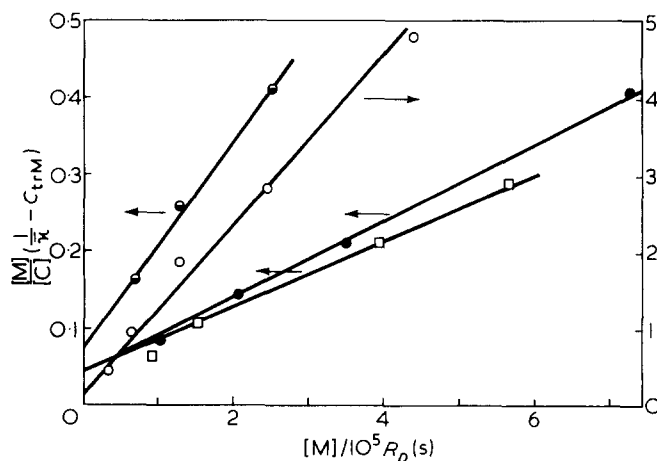


Figure 1 Kinetic analysis of the data obtained in the polymerization of styrene initiated by PAD (●), CAD (□), BAD (○) and PEAD (○)

preparation is high,  $f$  is nearly equal to that of AIBN and BPO and it does not have a cyano group and decomposes effectively under the usual polymerization conditions.

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