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Photopolymerization of Methyl Methacrylate Using 1-(N,N-Bis-Benzoylamino)-4,5-Diphenyl-1,2,3-Triazole as Photoinitiator

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PHOTOPOLYMERIZATION OF METHYL METHACRYLATE USING 1-(*N,N*-BIS-BENZOYLAMINO)-4,5-DIPHENYL-1,2,3-TRIAZOLE AS PHOTOINITIATOR

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ABSTRACT

1-(*N,N*-Bis-benzoylamino)-4,5-diphenyl-1,2,3-triazole (**1**) was used as the photoinitiator for the polymerization of methyl methacrylate in bulk and in solution. Polymerization in bulk follows the usual free-radical kinetics. The initiation is believed to occur via hydrogen abstraction from monomer or solvent caused by the excited state of **1**. Polymerization was found to be remarkably enhanced by the addition of a small amount of triethylamine. This was attributed to the formation of an electron transfer complex between photoactivated **1** and a ground-state amine.

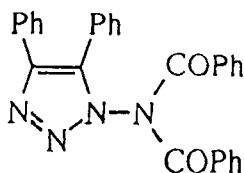
INTRODUCTION

The photoinitiated free-radical polymerization of vinyl monomers currently finds a growing application in printing inks, paints, and other coatings, generally designated as UV curing of coating [1, 2]. Critical to the success of such light-induced processes is the use of an efficient photoinitiator which is generally present in small amounts as an additive to the monomer system.

In this work, 1-(*N,N*-bis-benzoylamino)-4,5-diphenyl-1,2,3-triazole (**imide 1**, Structure **1**) was tried as a light-absorbing species because it was found [3] that irradiation of it ultimately leads to homolytic cleavage of the N—N bond and the

concomitant formation of the 1,2,3-triazolyl radical. The latter was considered capable of attacking the olefinic double bond of vinyl monomers. Methyl methacrylate was chosen as the monomer on the basis of its high reactivity toward radical-induced polymerization.

Imide 1



1

EXPERIMENTAL

Reagents

Methyl methacrylate (MMA) (from Merck) was treated with an aqueous sodium hydroxide solution, washed with water, dried over sodium sulfate, and finally vacuum distilled over cuprous chloride.

1-(*N,N*-Bis-benzoylamino)-4,5-diphenyl-1,2,3-triazole (1) was prepared by the thermal isomerization of 1-(α -benzoyloxybenzylideneamino)-4,5-diphenyl-1,2,3-triazole [4], which was obtained from the lead tetraacetate oxidation of benzil bis-benzoylhydrazone in methylene chloride [5]. The latter bis-hydrazone was prepared by refluxing benzil with benzhydrazide in ethanol solution [5]; 1 showed a melting point of 150–151°C.

α,α' -Azobisisobutyronitrile (AIBN) (from Fluka) was recrystallized from methanol. All solvents were analytical grade and used without further purification.

Photopolymerizations

Solutions of a known weight of MMA, photoinitiator, and solvent, if any, were charged into Pyrex tubes which were then stoppered and placed in a bath thermostated at 20°C. These solutions were illuminated by the light from a Hanovia 125-W medium pressure mercury arc lamp. Surrounding the lamp was a quartz well through which cooling water was pumped. The tubes were placed at a distance of 5 cm from the lamp. After irradiation for a given period of time, the polymer formed was isolated by precipitation in acidified cold methanol and centrifugation. The collected polymer was dried at 70°C under vacuum until a constant weight was obtained.

Measurements

Molecular weights (\overline{M}_n) of the polymers were obtained from viscosity measurements in benzene solution at 30°C by using the following relationship [6]:

$$[\eta] = 8.69 \times 10^{-5} \overline{M}_n^{0.76}$$

where $[\eta]$ is the intrinsic viscosity in dL/g.

The number-average degree of polymerization (\bar{P}_n) was calculated from the equation [7]

$$\log (\bar{P}_n) = 3.342 + 1.13 \log [\eta]$$

RESULTS AND DISCUSSION

Bulk Polymerization

1-(*N,N*-Bis-benzoylamino)-4,5-diphenyl-1,2,3-triazole (**1**) was found to be an efficient photoinitiator for the bulk polymerization of MMA. The results obtained by using various amounts of imide **1** (0.47 – $4.71 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) are shown in Table 1. Polymerizations had practically no induction time. No polymerization was observed in the absence of photoinitiator. When α,α' -azobisisobutyronitrile (AIBN) was used instead of imide **1**, under similar polymerization conditions, a lower rate of polymerization (R_p) was observed ($R_p = 3.31 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$ for **1** vs $R_p = 1.85 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$ for AIBN). Furthermore, with AIBN an induction time of about 10 minutes was needed.

As indicated in Table 1, R_p increased with increasing imide concentration. The dependence of R_p on [1] showed a reaction order of 0.5 (Fig. 1).

A plot of the reciprocal degree of polymerization ($1/\bar{P}_n$) against [1]^{0.5} gives a straight line passing through the origin (Fig. 2). These data clearly support a free-radical mechanism for the photopolymerization of MMA initiated by imide **1**, and the mode of termination is indicated to be bimolecular in nature. In Fig. 3 the reciprocal degree of polymerization ($1/\bar{P}_n$) is plotted against $R_p/[M]^2$. The absence of an intercept on the $1/\bar{P}_n$ axis indicates that monomer transfer reactions are negligible in the present polymerization. Therefore, the value of the kinetic parameter k_p^2/k_t can be evaluated with the help of the Mayo equation:

$$1/\bar{P}_n = (k_t/k_p^2) (R_p/[M]^2) ([2 + y]/[1 + y])$$

where y is the ratio of the rate constant for termination by combination (k_{tc}) to the rate constant for termination by disproportionation (k_{td}). Taking into account that $y = 0.44$ at 20°C [8], the above equation may be reduced to

$$1/\bar{P}_n = 1.69 (k_t/k_p^2) (R_p/[M]^2)$$

TABLE 1. Photopolymerization of MMA in Bulk Using Imide **1** as Photoinitiator at 20°C; [MMA] = $9.42 \text{ mol}\cdot\text{L}^{-1}$

[Imide] $\times 10^3 \text{ mol}\cdot\text{L}^{-1}$	$R_p \times 10^4 \text{ mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$	$[\eta]^a \text{ dL/g}$	\bar{M}_n	$1/\bar{P}_n \times 10^3$
4.71	0.2110	0.25	35,600	2.179
2.82	0.1821	0.37	59,600	1.399
0.94	0.0981	0.49	86,300	1.019
0.47	0.0769	0.76	153,700	0.620
0.47 ^a	0.1241			

^aTriethylamine (Et₃N) was also added; [Et₃N] = $4.71 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$.

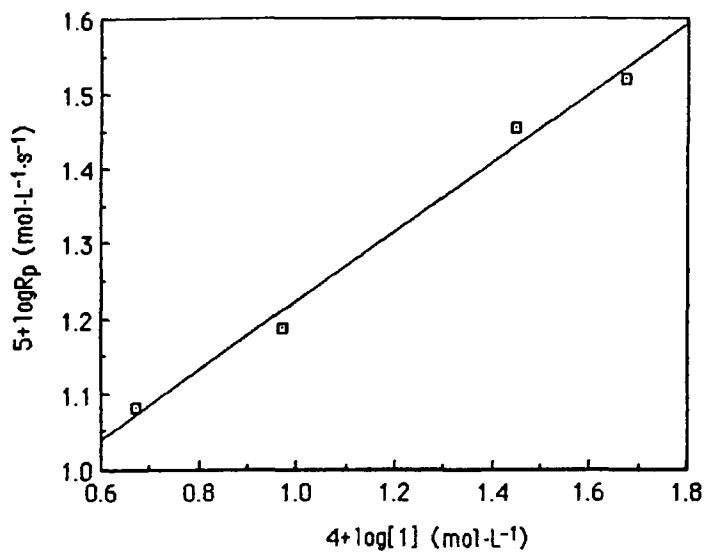


FIG. 1. Dependence of the rate of polymerization (R_p) of MMA on the concentration of photoinitiator 1; $[\text{MMA}] = 9.42 \text{ mol}\cdot\text{L}^{-1}$.

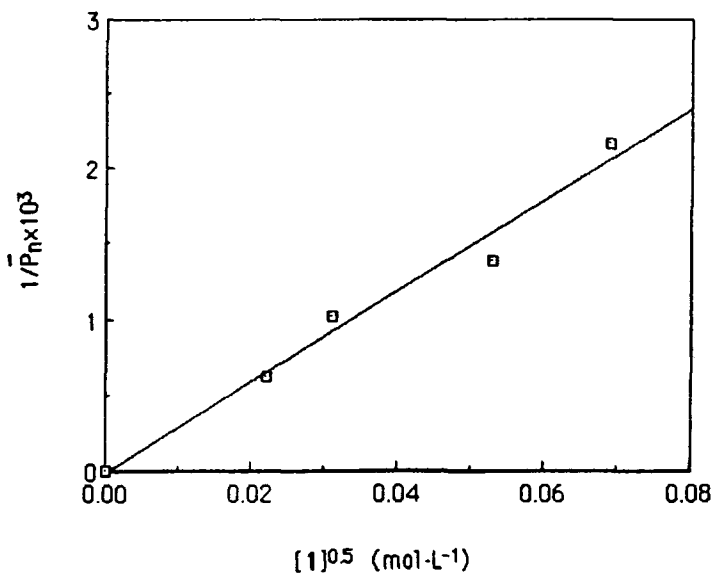


FIG. 2. Plot of reciprocal number-average degree of polymerization $1/\bar{P}_n$ vs square root of initiator 1 concentration.

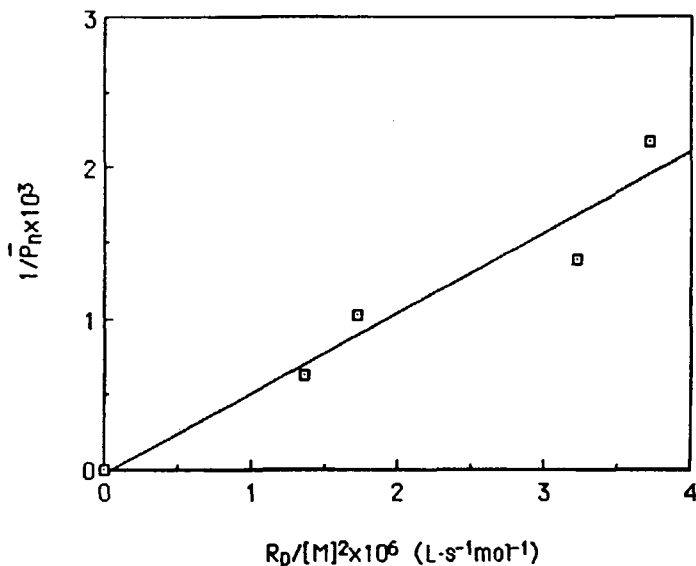


FIG. 3. Plot of $1/\bar{P}_n$ vs ratio of R_p over squared monomer concentration $[M]^2$.

The value of k_p^2/k_t can then be evaluated from the slope of a plot of $1/\bar{P}_n$ against $R_p/[M]^2$ (Fig. 3). This value was found to be $0.31 \times 10^{-2} \text{ L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, which is close to the literature value (0.23×10^{-2}) reported for MMA polymerization using AIBN as initiator at 20°C [9].

The photopolymerization of MMA induced by imide **1** was enhanced in the presence of triethylamine (Et_3N) (Table 1) but was strongly inhibited in the presence of hydroquinone. With 0.05% hydroquinone, an inhibition period of about 4 hours was observed.

Solvent Effect

The photopolymerization experiments were also performed in the presence of a variety of solvents such as acetonitrile (MeCN), benzene (PnH), carbon tetrachloride (CCl_4), methanol (MeOH), and isopropyl alcohol (PriOH). The results obtained are shown in Table 2 and clearly indicate that the role of solvents in the present polymerization is wider than their merely acting as chain transfer agents. R_p values parallel the hydrogen-donating ability of the solvents [10]. The highest rates were observed in PriOH and MeOH, while the lowest was observed for MeCN, which is the poorest hydrogen-donating solvent. However, when Et_3N was added to the MeCN polymerization solution, a significant increase of R_p was noticed. The presence of Et_3N also caused an increase in the R_p of the solution in PriOH, but this increase was not as significant as in the case of MeCN (Table 2).

Mechanism

Kinetic data and inhibition of the studied photopolymerization by hydroquinone indicate a free-radical mechanism for the polymerization.

TABLE 2. Solution Photopolymerization of MMA Induced by Imide 1 in Various Solvents; $[MMA] = 4.71 \text{ mol}\cdot\text{L}^{-1}$, $[Imide] = 4.71 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$

Solvent	$R_p \times 10^4$ $\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$	η_{inh}^a , dL/g
MeCN	0.14	0.24
MeCN + Et ₃ N ^b	1.05	—
PhH	0.35	0.21
CCl ₄	0.77	0.18
MeOH	1.09	0.18
PriOH	1.12	0.78
PriOH + Et ₃ N ^b	1.22	—

^aInherent viscosity (η_{inh}) was determined in methyl ethyl ketone at 25°C.

^bTriethylamine (Et₃N) was also added; $[Et_3N] = 7.06 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$.

The photochemical behavior of imide 1 was recently studied in our laboratory [3]. The UV absorption properties and fluorescence emission properties of 1 are shown in Table 3. Irradiation of the reaction mixture in a Pyrex vessel ($\lambda > 280 \text{ nm}$), as in the case of the studied polymerization, leads to preferential excitation of imide 1. The latter, most likely from its n, n^* triplet state [3], abstracts hydrogen from the monomer [11] or the solvent to give the semipinacol radical 2 and the corresponding monomer- or solvent-derived radical 3 (Scheme 1). Formation of the semipinacol radical 2 is followed by cleavage of the weak N—N bond in the β -position and leads to the 1,2,3-triazolyl radical 4 and the enol form of benzamide 5.

We consider this cleavage to be a key step with respect to the high photoinitiating ability of 1, because semipinacol radicals produced from benzophenone derivatives, when the latter are used as photoinitiators, have induced termination of polymerization to a considerable extent [12, 13].

While it is certain that the 1,2,3-triazolyl radical 4 can be efficiently quenched by hydrogen abstraction to yield 1(2)*H*-4,5-diphenyl-1,2,3-triazole (6) and radical 3, it is still possible that this heteroaromatic radical is also capable of addition to

TABLE 3. Absorption and Fluorescence Maxima of Imide 1 in Benzene and Acetonitrile^a

Solvent	Absorption		Emission, λ_{max} , nm
	λ_{max} , nm	log ϵ	
PhH	301	3.30	366
MeCN	312	3.21	400

^aTaken from Reference 3.

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