Organic Sulfur Compounds as Initiators of Polymerization. VII. Polymerization of Methyl Methacrylate by N-[(p-Benzoyl)benzenesulfonyl]benzenesulfonamide

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ABSTRACT: The photopolymerization of methyl methacrylate in bulk using N-[(p-benzoyl)benzenesulfonyl]benzenesulfonamide as a photoinitiator was studied. A kinetic study of the photopolymerization showed that the rate of polymerization is proportional to the square root of the photoinitiator concentration. The decomposition of a sulfur–nitrogen bond and the obtained radicals are suggested to be responsible for the initiation of polymerization. The influence of the photoinitiator on the molecular weight was also studied. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 2083–2086, 1998

Key words: photoinitiators; kinetics; photopolymerization

INTRODUCTION

Photoinduced radical or cationic polymerization of vinyl monomers has become increasingly important in recent years, mainly because of the extensive application of these processes in photoactive polymer-based systems, i.e., UV cured paints, printing inks, and printed coatings and in three-dimensional stereolithography and holographic recordings. Many efficient photoinitiators have been developed and some of them are commercially available. Among them are sulfur-containing compounds: sulfides[2,3] ketosulfides,[1,4,5] sulfonates,[6,7] sulfonium salts,[8,9] sulfurazo compounds,[10–12] and thioxanthones.[13,14] An ideal commercial photoinitiator is expected to exhibit many properties: 1) easy synthesis and low price, 2) absence of toxicity, 3) excellent shelf stability and pot life when dissolved in reactive monomers, and 4) high absorption of incident light.

The latest articles were devoted to sulfur-containing initiators: S(4-benzoyl)phenylthiobenzoate,[1] sodium-4-phenyl-phenylthiosulfonate,[15] diphenyl ester of diphenyl-4-thiosulfonic acid,[16] N-4-benzoylphenylsulfonyl-N-methylbenzenesulfonamide,[17] phenylazo-4-diphenylsulfone, phenylazo-4-diphenylthiosulfone, and phenylazo-4-diphenylsulfide.[12,18]

The purpose of this article was the study of methyl methacrylate (MMA) polymerization by a new sulfur-containing photoinitiator, N-[(p-benzoyl)benzenesulfonyl]benzenesulfonamide. The photoinitiator has the benzophenone chromophore which is a strong triplet sensitizer (i.e., the quantum yield of phosphorescence is equal to 1) and is soluble both in organic solvents and in water.

EXPERIMENTAL

The electronic absorption spectra were recorded with UV-vis Carry 3 absorption spectrometer and IR spectra were conducted using an FTIR spectrometer, Model 1650 Perkin–Elmer. The UV irradiation at the position of sample was measured

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For Part VI of this study, see Ref. 1.

using an IL 1400 A Int. Light Inc. USA radiometer at 40 mW/cm^2. Polymer molecular weights were determined in tetrahydrofuran with a Waters HPLC Model with reference to polystyrene standards. Mass spectra (field desorption) were taken with a Varian MAT 711 spectrometer. Semiempirical calculations were performed by the AM-1 method.

Synthesis

A mixture of 1.57 g (0.01M) benzenesulfonamide, 4.0 g (0.01M) 4-benzoyl-benzenesulfonchloride, and 1.56 g (0.02M) anhydrous potassium carbonate, and 50 cm^3 of xylene was heated at boiling temperature for 1 h. The precipitate N-[(p-benzoyl)benzenesulfonyl]benzenesulfonimide potassium salt after cooling was filtered off dissolved in water, acidified with concentrated HCl, and recrystallized from ethanol.

Yield of reaction 80% mp. 147–149°C. MS m/z (relative intensity) 401 (M$^+$ 13). IR (KBr) cm^{-1}: 1655 (CO), 1370, 1164 (SO$_2$), 3163 (NH).

Photopolymerization

Methyl methacrylate (MMA) from Aldrich was washed three times with portions of 5% aqueous sodium hydroxide to remove the inhibitor and then twice with distilled water. The monomer, dried over anhydrous MgSO$_4$, was then distilled under reduced pressure before using. Photopolymerization efficiencies were determined gravimetrically by irradiation with a quartz cell apparatus containing 3 cm^3 MMA and the photoinitiator. After irradiation, the reaction mixture was poured into methanol for precipitation, and this was followed by filtering and drying to a constant weight in a vacuum oven at 50°C. The photopolymerization rates (R_p) were calculated as the slopes of the initial straight portion of the percent conversion versus irradiation time. The light source used was a xenon lamp (150 W). The water filter was used to cut off the heat emitted by the source of irradiation. All solutions were deoxygenated by bubbling high-purity nitrogen through them.

RESULTS AND DISCUSSION

UV Absorption Spectra

The investigated photoinitiator consists of major bands, one maximizing at 261 nm ($\varepsilon = 18\,200$

L mol^{-1}) and the other at 339 nm ($\varepsilon = 190$) in cyclohexane. The low value of ε_{max} for the longer wavelength band allows the assignment of the $n \rightarrow \pi^*$ orbital transition to this band. The value ($\varepsilon_{max} = 18,200$) of the short-wavelength band allows the assignment of the $\pi \rightarrow \pi^*$ orbital transition to this band. Figure 1 shows that light irradiation of the photoinitiator in water results in a substantial decrease of the band intensities at 261 nm and indicates that decomposition of the photoinitiator takes place. The literature data shows that the sulfur–nitrogen bond is the weakest one in the molecule and can be broken on light irradiation.[19–21]

N-[(p-Benzoyl)benzenesulfonyl]benzenesulfonamide contains two different S—N bonds. However, semiempirical calculations by the AM-1 method indicate that the S—N bond distances are 1.65 and 1.64 Å, that is, they are almost identical. The calculations are in good agreement with the crystal structural data.[22] Therefore, one can expect that photocleavage occurs as follows:
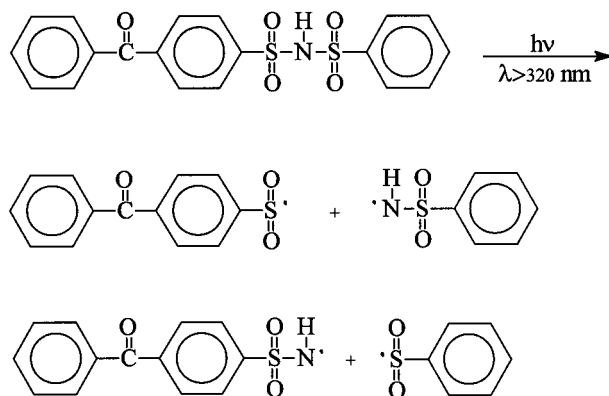
Effect of Initiator Concentration on the Rate of Polymerization

N-[p-(Benzoyl)benzenesulfonyl]benzenesulfonamide has been found to be an effective photoinitiator in the polymerization of MMA. The initial polymerization rate (R_p) varies linearly with the square root of the photoinitiator concentration up to $8 \cdot 10^{-3}$ M (Fig. 2). As the concentration of the photoinitiator increases beyond $8 \cdot 10^{-3}$ M, the rate of polymerization decreases, indicating that the chain-terminating or chain-transfer reactions are so small at a low concentration of the photoinitiator that the polymerization proceeds by the ordinary radical scheme. In the concentration beyond $8 \cdot 10^{-3}$ M, the rate of polymerization does
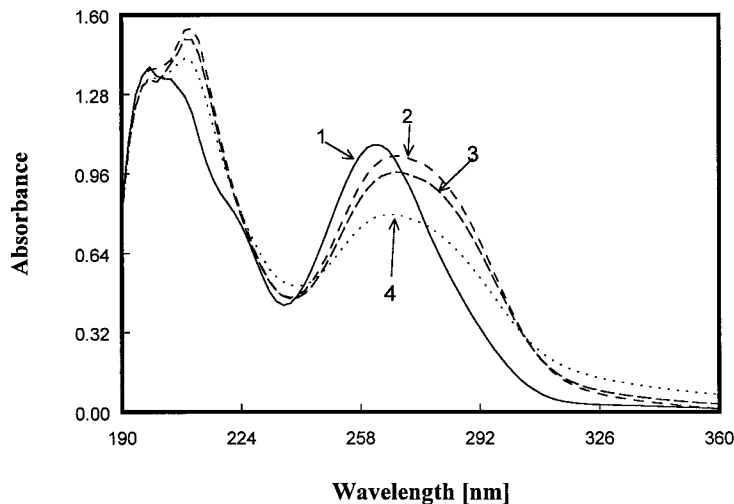
Figure 1   Absorption spectra of the photoinitiator in water (1) before and after (2) 15 min, (3) 60 min, and (4) 240 min of irradiation.

not depend linearly on the square root of the photoinitiator concentration. These results indicate that the photoinitiator acts as both a photoinitiator and a terminatior of the polymerization and the chain-transfer and -termination reactions are not negligible at a high photoinitiator concentration.

Figure 3 shows a plot of the (chain length)$^{-1}$ versus the rate of polymerization. The intercept on the ordinate of Figure 3 is equal to k_f/k_p, where k_f represents the velocity constant for transfer to the monomer and k_p is the velocity constant for chain growth. The value for k_f/k_p is about 10^{-4}, indicating that, on average, one transfer reaction occurs for 10^4 propagation reactions; in the poly-
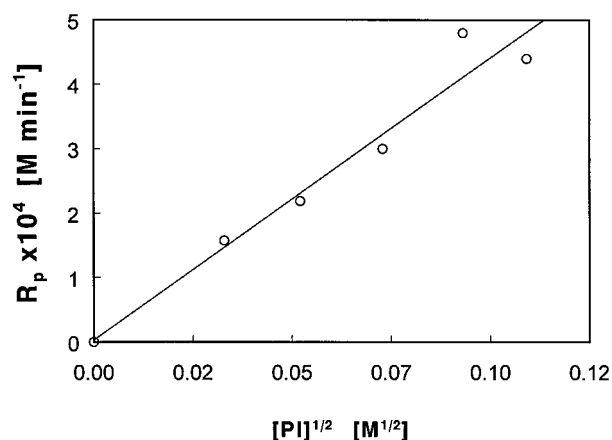
merizations carried out, therefore, the transfer to monomer can be neglected.

Molecular Weights

MMA polymers with a molecular weight $>10^5$ were obtained in these experiments. The time of irradiation was in all cases the same and equal to 35 min. The dependence of the number-average molecular weight ($\bar{M}_n$), the weight-average molecular weight ($\bar{M}_w$), the polydispersity index ($\bar{P} = \bar{M}_w/\bar{M}_n$), and the number-average polymerization degree ($\bar{X}_n$) on the concentration of the photoinitiator (PI) is shown in Table I. In this concentration range, the relationship between the reciprocal molecular weight and N - [(p - benzoyl)benzenesulfonyl]benzenesulfon - amide is linear with respect to $(PI)^{1/2}$ for $\bar{M}_n$. This

Figure 2   Initial polymerization rate (R_p) of MMA as a function of the square root of the photoinitiator concentration ($[PI]^{1/2}$).
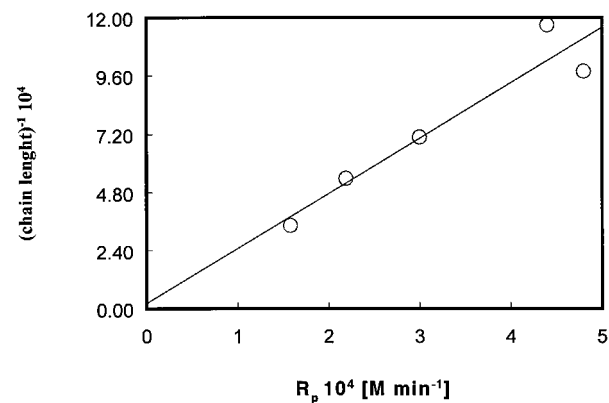

Figure 3   Dependence of (chain length)$^{-1}$ versus rate of polymerization.

Table I Dependence of the Number-average Molecular Weight ($\overline{M_n}$), Weight-average Molecular Weight ($\overline{M_w}$), Polydyspersity Index (P), and Number-average Polymerization Degree ($\overline{X_n}$) on the Photoinitiator Concentration t_{IRR} = 35 min

$c[M]$	$\overline{M_n}$	$\overline{M_w}$	P	$\overline{X_n}$
0.0010	289,813	600,988	2.07	2898.13
0.0025	185,185	372,221	2.01	1851.85
0.0050	141,546	298,163	2.10	1415.46
0.0080	102,256	225,641	2.20	1022.56
0.0110	85,271	216,988	2.54	852.71

is in agreement with the R_p dependence on $(PI)^{1/2}$. The polydispersity index is close to 2.10.

CONCLUSION

The results indicate that N-[(p-benzoyl)benzenesulfonyl]benzenesulfonamide is an effective initiator of the photopolymerization of MMA. Because the photoinitiator has a benzophenone chromophore which is a strong triplet sensitizer, it is expected to polymerize most effectively monomers that do not quench the triplet state of the photoinitiator.[23]

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