

THE PHOTOPOLYMERIZATION OF MMA INITIATED BY 3-ARYLOYLCOUMARIN COMPOUNDS*

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ABSTRACT

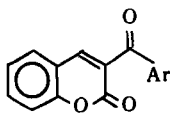
A bulk photopolymerization of methyl methacrylate (MMA) initiated by 3-benzolocoumarin (Sen. 1) — triethylamine (TEA) cointiated has been studied. Results were compared with a well known photoinitiator system, benzophenone (BP) — TEA. The mechanism of the reaction has been discussed.

INTRODUCTION

Recently, 3-aryloylcoumarins as an effective photoinitiator or photosensitizer for polymer photocrosslinking have received extensive attention.^[1,2,3] Williams et al.^[2] have investigated the ability of photoinitiating polymerization of these compounds in the polymer thin films. However, the photoinitiating mechanism and behaviour of these compounds in solution have not yet been reported. In this work, we studied the bulk photopolymerization of methyl methacrylate (MMA) taking 3-benzolocoumarin (Sen. 1) — triethylamine as initiators. The experimental results were compared with a conventional photoinitiating system BP — TEA.

EXPERIMENTAL

3-Aryloylcoumarin was synthesized in our lab^[3], and the structure is as follows:



Ar is benzene (Sen. 1), α -furan (Sen. 2), α -thiophene (Sen. 3), 4-(3-coumarin) benzoyl (Sen. 4), 3-coumarin (Sen. 5).

MMA, commercial reagent, was distilled fractionally before use for polymerization.

The absorption spectra were recorded on a UV spectrophotometer mode 330, phosphorescence spectra and lifetime of these compounds were measured on a Hitachi MPF-4 spectrofluorimeter.

Photopolymerization of MMA was carried out in dilatometers (10mm) at 20°C. A 250 W high-pressure mercury lamp was used as the light source and short wavelength (less than 300 nm) UV light was removed by the pyrex glass filter.

RESULTS AND DISCUSSION

Polymerization rates were measured by conventional dilatometric technique. In the presence of sensitizer—Sen. 1, if there is no TEA, the polymerization of MMA did not occur. However when Sen.

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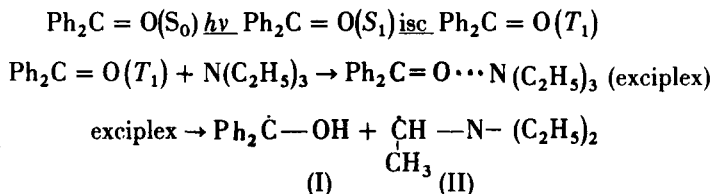
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1/TEA coinitiator system was used, the polymerization of MMA can be initiated. It indicated that Sen. 1 was found to be an effective photosensitizer for bulk polymerization of MMA at 20°C. Table 1 indicates that initial rates of polymerization were determined for each sensitizer as a function of [Sen.], the data being corrected for the rate of polymerization in the presence of sensitizer.

Table 1 The rates of polymerization of MMA initiated by Sen 1/TEA and BP/TEA

Number	Sen.1/TEA/MMA			BP/TEA/MMA		
	Sen.1 $\times 10^4 M$	TEA M	R_p $\times 10^2 M.S.$	BP $\times 10^4 M$	TEA M	R_p $\times 10^2 M.S.$
1	5.0	0.04	1.13	90	0.04	0.50
2	5.0	0.04	1.13	5.0	0.04	0.26

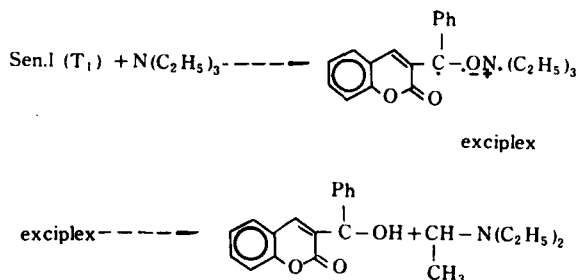
BP has become the most widely used sensitizer for organic photochemistry^[4], and its photochemical and photophysical characteristics have been studied extensively. BP has the lowest energy electronic transfer of $n-\pi^*$ character.



In the above scheme, radical II has high reactivity and therefore it can initiate the polymerization of MMA. However, radical I is not only formed at room temperature, but also terminates the process of polymerization⁽⁵⁾.

As shown in Table 1, Sen. 1 is apparently a better photoinitiator for MMA polymerization than BP. The possible reasons are: (1) the intersystem crossing efficiency of photoinitiator Sen. 1 is very high (0.92); (2) the lowest triplet of Sen. 1 is of $n-\pi^*$ character; (3) Sen. 1 triplet energy, $E_t = 58.6$ kcal/Mol. while BP triplet energy, $E_t = 69$ kcal/Mol., which is close to that of MMA. Therefore the excited BP is easier to be quenched by MMA.

It is considered that the photoreduction of studied compounds is similar to that of BP. The mechanism can be shown as follows:



It is seen that the triplet energy of Sen. 1 is lower than that of MMA, and the photosensitization cannot occur by direct energy transfer to monomer, but the triplet energy of BP is higher, the excited state molecule is quenched by energy transfer to monomer more or less. Furthermore, the triplet energy of BP is also higher than that of styrene ($E_t = 61.5$ kcal/Mol) or butadiene ($E_t = 60$ kcal/Mol). While the triplet energy of the studied sensitizers is lower. So, it is expected that these sensitizers can initiate the polymerization of styrene or butadiene which can not be induced by BP.

Keywords:

Photopolymerization; 3-Aryloylcoumarin; Sensitizer

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