

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Solid-state Photoinduced Polymerization of 3-Methoxy-4-benzyloxystyrene

J. M. Rooney^a

^a Loctite (Ireland) Ltd., Tallaght, Ireland

To cite this Article Rooney, J. M.(1986) 'Solid-state Photoinduced Polymerization of 3-Methoxy-4-benzyloxystyrene', *Journal of Macromolecular Science, Part A*, 23: 7, 823 – 829

To link to this Article: DOI: 10.1080/00222338608069474

URL: <http://dx.doi.org/10.1080/00222338608069474>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Solid-State Photoinduced Polymerization of 3-Methoxy-4-benzyloxystyrene

J. M. ROONEY

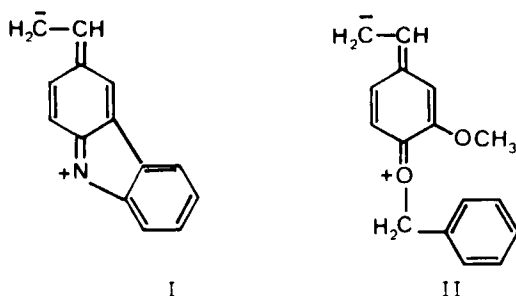
Loctite (Ireland) Ltd.
Whitestown Industrial Estate
Tallaght, Ireland

ABSTRACT

The photoinduced polymerization of 3-methoxy-4-benzyloxystyrene (MBS) in the solid state has been studied by infrared spectroscopy, liquid chromatography, and scavenging experiments. In the absence of added photoinitiator, polymerization rates were found to accelerate as polymerization progressed. Reaction products consisted of unreacted MBS, dimer, and high-molecular-weight polymer. The polymerization was shown to proceed by a free-radical mechanism.

INTRODUCTION

Although numerous observations of solid-state cationic polymerizations induced by high energy (i.e., gamma) radiation have been made [1-5], reports of such polymerizations being initiated by lower-energy (ultraviolet) radiation in the absence of a photosensitizer are rare [6]. A zwitterion (I) has been proposed as a transient intermediate in the UV-initiated solid-state cationic polymerization of 9-ethyl-3-vinyl carbazole (3VC).



Recent work in these laboratories has demonstrated the high reactivity of 3-methoxy-4-benzoyloxystyrene (MBS) in cationic polymerizations [7], and preliminary experiments indicated that crystalline MBS polymerizes on exposure to ultraviolet light without the addition of photoinitiator. In principle, MBS is capable of forming a zwitterionic structure (II) analogous to I. The present study was undertaken to determine the mechanism of the solid-state photoinduced polymerization of MBS.

EXPERIMENTAL

MBS (Aldrich) was purified by recrystallization from petroleum ether to give spectroscopically and chromatographically pure material (mp 50–51°C). The cationic photoinitiator 2,4,6-triphenylpyrylium hexafluoroantimonate (TPPH) was synthesized according to the general procedure of Ketley and Tsao [8] and purified by repeated recrystallization from acetone and dichloromethane. Ethyl *p*-dimethylamino-benzoate (EPD), 2,2-dimethoxy-2-phenylacetophenone (DMPA), and 2,6-di-*t*-butyl-4-methylphenol (DBMP) were used as received without further purification.

Polymerizations were conducted at ambient temperature ($\sim 20^\circ\text{C}$) by exposing 50- μm films of MBS with or without additives to the output from a Lumatec UVL 216 liquid lightguide attached to a Lumatec S-UV 201 A ultraviolet light source containing a high-pressure mercury arc fitted with heat filters. Radiation intensities were measured with an OAI Model 206 UV Powermeter (Optical Associates, Inc.). MBS films were prepared by evaporative recrystallization of the monomer from a variety of solvents including dichloromethane, petroleum ether, and acetone. Where additives were employed, solutions of MBS and the additive were cocrystallized. Films were exposed on either glass slides or sodium chloride infrared spectroscopy plates, usually in air. In some experiments a nitrogen-purged vessel enclosed the lightguide and the film with its substrate. Consumption of MBS was estimated from the diminution in relative intensity of the IR band at 1625 cm^{-1} ,

using the baseline density method [9]. Polymerization mixtures were analyzed on a Waters 244 liquid chromatograph equipped with μ -Styragel columns.

RESULTS

Exposure of pure MBS to ultraviolet radiation produced rapid reductions in the intensities of the infrared bands at 3 085, 1 625, and 900 cm^{-1} associated with the vinyl group of the monomer. The rate of reduction increased with increasing radiation intensity as measured at 365 nm (see Fig. 1). Analysis of the irradiated material by liquid chromatography showed that only monomer, dimer, and polymer with a molecular weight in excess of 10 000 were present, as illustrated in Fig. 2. Irradiation of MBS in a nitrogen atmosphere only marginally increased the rate of monomer consumption (see Fig. 3). Insertion of a Pyrex filter between the light guide and the MBS resulted in a long induction period before MBS consumption commenced.

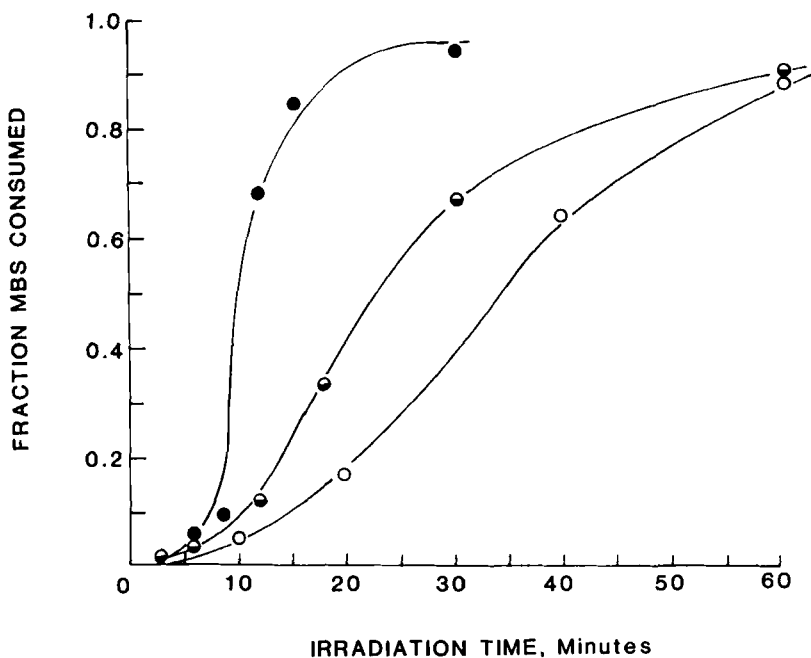


FIG. 1. Relative rates of MBS consumption in air at radiation intensities of (●) 135, (◐) 96, and (○) 58 mW/cm^2 measured at 365 nm.

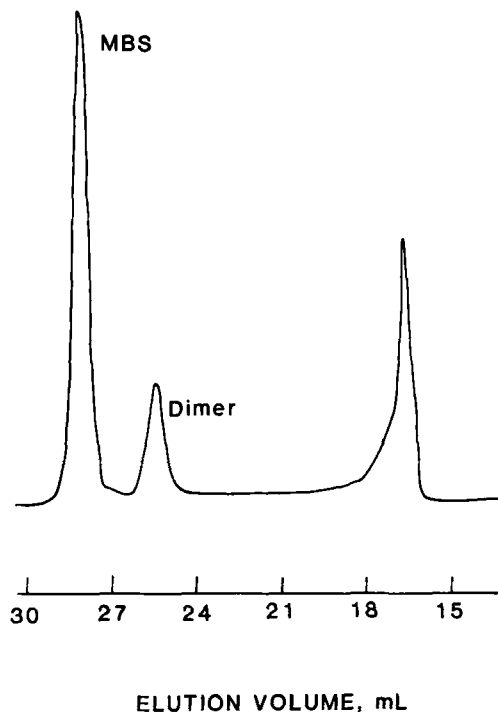


FIG. 2. Gel permeation chromatogram for products of MBS irradiated at 165 mW/cm^2 for 10 min in air. (Eluent, CH_2Cl_2 ; columns, 500 \AA and $2 \times 100 \text{ \AA}$ μ -Styragel).

Experiments were then conducted in which additives were mixed with MBS. Solid mixtures were irradiated for 15 min at 135 mW/cm^2 , and the extent of MBS consumption was estimated by IR spectroscopy. While an additive-free control sample and a sample containing 10% EPD gave almost identical results (85 and 86% MBS consumption, respectively), a sample containing 10% DBMP showed only 20% MBS consumption.

In another series of experiments, the product distributions in an irradiated pure MBS control sample and in samples containing 2% DMPA or 2% TPPH were compared. On irradiation, the DMPA-containing sample gave a GPC trace similar to that of the control, as shown in Fig. 4. However, the GPC trace of the TPPH-containing sample indicated the virtual absence of dimer and the presence of a large amount of low molecular weight polymer.

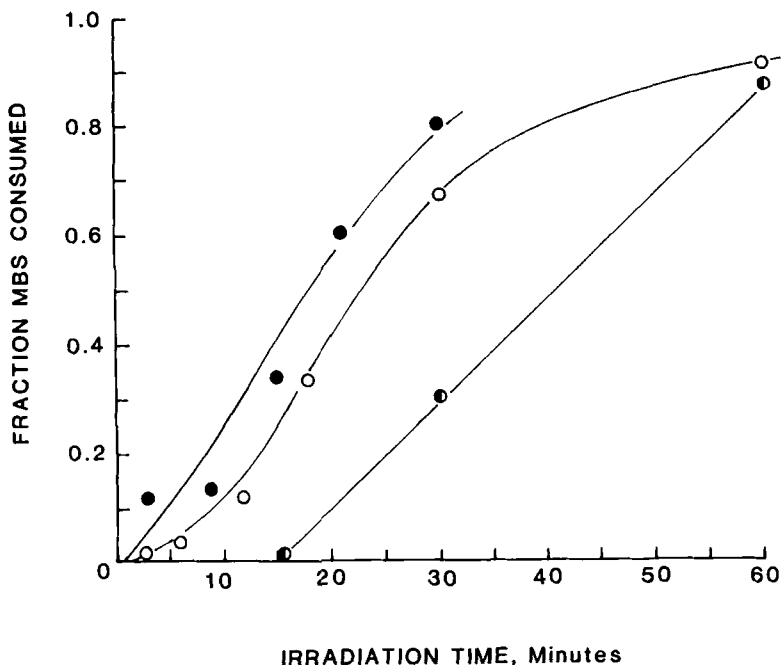


FIG. 3. Relative rates of MBS consumption at nominal radiation intensity of 96 mW/cm^2 (●) under nitrogen atmosphere, (○) in air, and (●) in air with a Pyrex filter.

DISCUSSION

Since photoinduced MBS polymerizations were conducted at a temperature approximately 30°C below the melting point of the monomer, the reactions appear to proceed in the solid state. However, arguments have been presented which suggest that localized melting may occur in the vicinity of propagating centers due to the reaction exotherm and that, although the bulk of the monomer remains solid, propagation may occur in liquid microphases [1]. An alternative hypothesis attributes increased molecular mobility to the presence of crystal defects which have been shown to assist polymerization. As the extent of polymerization increases, the number of these defects should multiply [4]. Either of these hypotheses could account for the rate acceleration which has been observed in radiation-induced solid-state vinyl polymerizations. Rate curves of the photoinduced polymerization of MBS also show this effect (see Figs. 1 and 3), which by analogy may be ascribed to the same possible causes.

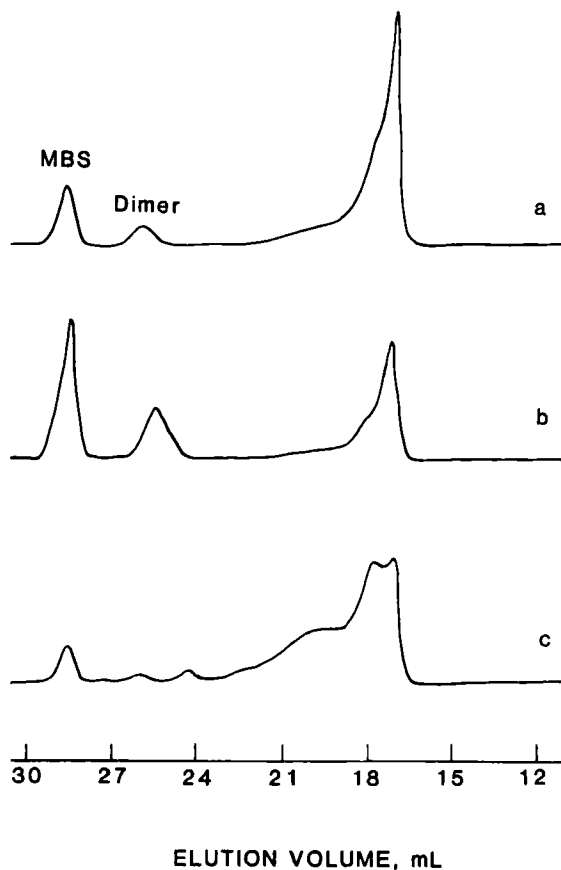


FIG. 4. Gel permeation chromatograms for products of MBS irradiated at 135 mW/cm^2 for 10 min: (a) MBS + 2% DMPA, (b) pure MBS, and (c) MBS + 2% TPPH.

Irradiation of MBS in the absence of photoinitiator yields a product distribution similar to that reported for polymerizations of 3VC: saturated dimer is formed as a by-product along with high-molecular-weight polymer [6]. When solid mixtures of MBS and DMPA, a free-radical photoinitiator, are irradiated, the product distribution remains unchanged although the rate of monomer consumption increases greatly. On the other hand, replacement of the DMPA by TPPH, a cationic photoinitiator, causes very different polymerization behavior. Once again, the rate of MBS consumption is increased, but the formation of dimer is suppressed and polymer molecular weights are lowered. In addition, the irradiated film shows a slight pink color due to

the formation of cyclized terminal groups observed in solution cationic polymerizations of MBS [7]. These results imply a radical mechanism for the photoinduced solid-state polymerization of MBS in the absence of added photoinitiator.

Support for this conclusion can be drawn from experiments with scavengers. The rate of polymerization is depressed markedly by DBMP, a known free-radical scavenger. Addition of EPD, an amine, fails to reduce the polymerization rate. Amines are known to inhibit vinyl cationic polymerizations.

The only evidence which appears contradictory is the absence of any retarding effect of oxygen on the polymerization rate. This observation has been adduced as support for a cationic mechanism in the case of 3VC polymerizations [6]. However, oxygen has been shown to increase the rate of N-vinylcarbazole consumption during the radiation-induced solid-state polymerization of this monomer [10], which has been shown to proceed by a free-radical mechanism [11].

REFERENCES

- [1] J. Westlake and R. Y. Huang, J. Polym. Sci., Polym. Chem. Ed., **10**, 2149 (1972).
- [2] A. S. Chawla and L. E. St. Pierre, Ibid., **10**, 2691 (1972).
- [3] V. Jaacks, K. Boehlke, and W. Kern, Makromol. Chem., **165**, 51 (1973).
- [4] A. S. Chawla and R. Y. Huang, Ibid., **176**, 2669 (1975).
- [5] J. J. Lebrun, A. Deffieux, P. Sigwalt, A. Wang, and V. Stannett, Radiat. Phys. Chem., **24**, 239 (1984).
- [6] S. Tazuke, O. Supakorn, and T. Inoue, J. Polym. Sci., Polym. Chem. Ed., **20**, 2239 (1982).
- [7] J. M. Rooney, Polym. Commun., In Press.
- [8] A. D. Ketley and J.-H. Tsao, J. Radiat. Curing, **6**, 22 (1979).
- [9] A. van Neerbos, J. Oil Colour. Chem. Assoc., **61**, 241 (1978).
- [10] W. Pekala and A. Lesinski, Nukleonika, **19**, 769 (1974).
- [11] W. Pekala and A. Lesinski, Ibid., **24**, 613 (1979).

Received April 18, 1985