

# Photocrosslinking of Poly (Allyl Methacrylate)

## Prepared By Group Transfer Polymerization

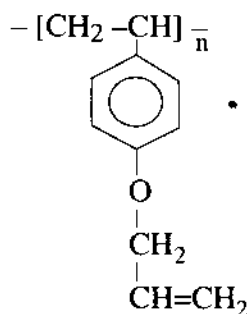
Aysen ÖNEN, Huçeste GİZ and Yusuf YAĞCI  
 İstanbul Technical University, Department of Chemistry  
 Maslak, İstanbul 80626-TURKEY

Received 3.2.1993

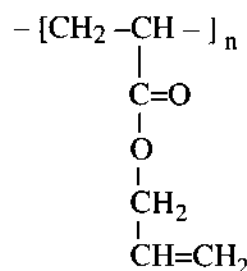
Linear polymers with pendant allyl groups were prepared by group transfer polymerization of allyl methacrylate. Photocrosslinking reaction of poly(allyl methacrylate) using benzophenone and benzoin methyl ether are compared and discussed in terms of photocrosslinking mechanism.

### Introduction

Photocrosslinking of polymers find increasing interest because of its application in photoresist technology<sup>1</sup>. This process is based on the simultaneous formation of insoluble networks upon irradiation of polymers with functional groups in the presence of photoinitiator or photosensitizer. Typical examples include polymers having cinnamate, acrylate, epoxy, propargyl, allyl and vinyloxy moieties in the side chain as functional groups. Linear polymers having allyl side chains can not be prepared by radical polymerization because of the reactivity of both vinyl and allyl groups. Kato et. al.<sup>2,3</sup> prepared soluble high molecular weight poly(allyl-4 vinyl phenyl ether) by cationic polymerization because the vinyl group alone polymerized selectively. On the other hand, by radical polymerization, the linear polymer with lower molecular weight was obtained only at a relatively low polymerization ratio. Another structurally related monomer, allyl methacrylate (AMA) does not polymerize by cationic mechanism.

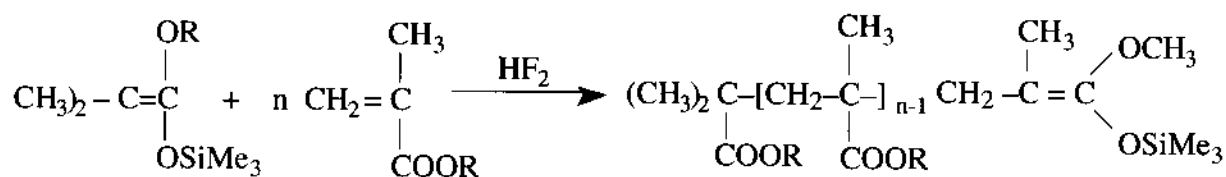


Poly (allyl-4-vinyl phenyl ether)



Poly (allyl methacrylate)

Group transfer polymerization (GTP) is a new polymerization method which results in linear and monodisperse polymers. The polymerization involves Michael addition of a silyl ketene acetal initiator to  $\alpha,\beta$ -unsaturated esters, ketones and nitriles.



This method bears a strong resemblance to anionic polymerization. Both techniques are useful for the same monomer, they have almost identical enthalpies and entropies of activation and produce polymers with similar tacticities. However GTP reactions are extremely rapid and it is possible to work at high temperatures. Since GTP follows a certain polymerization route it is possible to polymerize some special monomers such as AMA which can not be polymerized with radical mechanism.

This paper presents photocrosslinking reactions of poly(allyl methacrylate) (PAMA) prepared by GTP.

## Experimental

**Materials:** Allyl methacrylate (AMA), and THF were purified by conventional drying and distillation procedures. 1-Methoxy-2-methyl-1-trimethylsilyloxypropane (MTS), tris(dimethyl amino) sulphonium bifluoride (Tashf<sub>2</sub>), acetonitrile, benzoin methyl ether (BME) and benzophenone (BP) (commercial products) were used as purchased.

**Polymerization of AMA:** Previously purified AMA (20 ml), MTS (0.1 ml) and dry THF were mixed together under an atmosphere of dry nitrogen. The catalyst (Tashf<sub>2</sub>) was then added as a solution (0.1 M) in acetonitrile. The mixture immediately warmed and was stirred until it cooled. The polymer was recovered after precipitation into methanol-water mixture.

**Photocrosslinking of PAMA:** 0.1 g of PAMA and  $1.65 \times 10^{-1}$  mol/lit BME or BP was dissolved in 0.5 ml of CH<sub>2</sub>Cl<sub>2</sub> and outgassed in a high vacuum system. This solution was irradiated in an Annular Photoreactor (Applied Photophysics) emitting light nominally at  $\lambda = 350$  nm. Photocrosslinking time was noted as the time required for complete gelation. Several experiments were also performed in films which were casted from solution by evaporating the solvent.

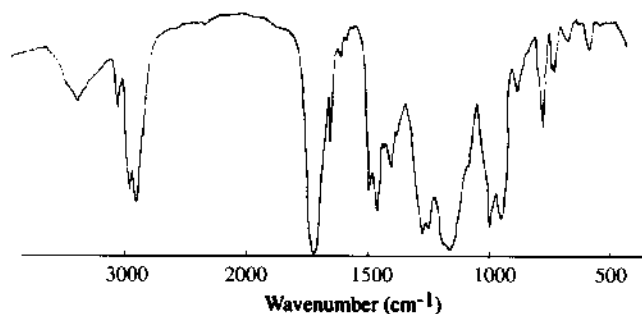
**Analysis:** IR spectrum was taken on a Jasco FT-IR 5300 spectrometer. GPC chromatograms were taken on a Knauer M 64 type instrument, using tetrahydrofuran as an eluent with a flow rate of 1 ml/min. and molecular weights were calculated according to polystyrene standards.

## Results and Discussion

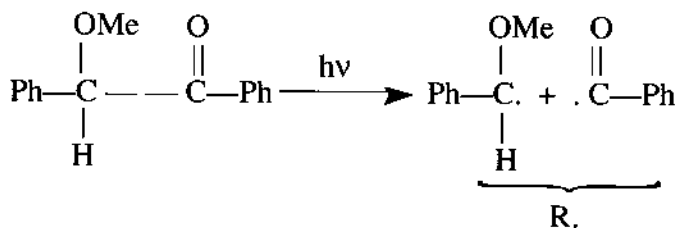
AMA was polymerized by GTP polymerization. Table 1 contains the polymerization conditions and the results of polymerization of AMA. The resulting polymers were soluble in organic solvents such as THF, toluene, CH<sub>2</sub>Cl<sub>2</sub> etc. which are also solvents for the analog poly(methylmethacrylate). For information on polymerization behaviour, the infrared spectra of these polymers were investigated. The infrared spectrum of (1) (Figure 1) has strong absorption bands in the region of 925 and 985 cm<sup>-1</sup> which might be attributable to the double bond in the allyl group<sup>2</sup>. These results indicate that polymerization takes place through the vinyl double bond without affecting the allyl double bond.

**Table 1.** Polymerization of allyl methacrylate

Code	AMA (mol/l)	MTS (mol/l)	Tashf <sub>2</sub> (mol/l)	THF (mol/l)	Conversion (%)	$\bar{M}_n$	$M_w/M_n$
1	6.99	0.023	0.004		37	13570	1.692
2	6.99	0.023	0.004		65	29610	2.227
3	2.07	0.006	0.001	8.69	50	14350	1.389
4	4.72	0.015	0.003	9.93	83	-	-


**Figure 1.**

Photocrosslinking of these polymers using photosensitizers is compared in Table 2. As clearly shown, when no sensitizer is used, the sensitivity of PAMA was quite low. However when the photosensitizer was used, the photocrosslinking reaction of PAMA is accelerated. Among the photosensitizers tested BME seems to be the most effective. In this case, crosslinking reactions occur via photogenerated radicals formed upon irradiation.

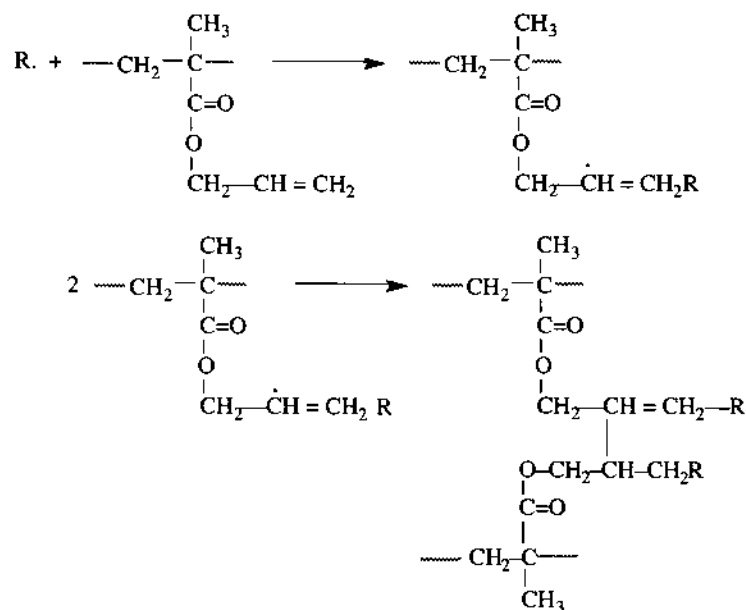

**Table 2.** Photocrosslinking of poly(allylmethacrylate) in CH<sub>2</sub>Cl<sub>2</sub> at  $\lambda = 360$  nm

Photosensitizer <sup>a</sup>	PAMA (g/l)	Gelation time (min.)
None	100	> 300 <sup>b</sup>
Benzoin methyl ether	300	40
Benzophenone	300	60
Benzophenone <sup>c</sup>	300	40

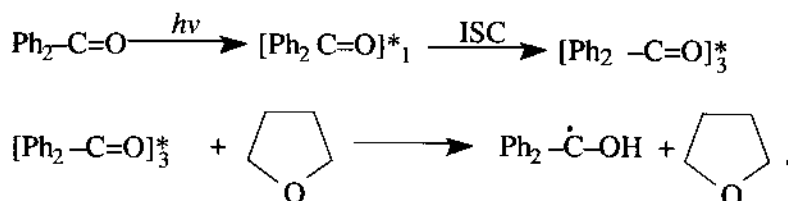
<sup>a</sup> [Photosensitizer] =  $1.65 \times 10^{-1}$  mol / l.

<sup>b</sup> No gelation was observed at this time.

<sup>c</sup> in THF



In the case of BP, photocrosslinking radicals are generated by hydrogen abstraction of excited BP. Photocrosslinking was substantially accelerated when THF, a powerful hydrogen donor<sup>6</sup>, was added to the system.



We have also prepared films of PAMA on glass plates under similar conditions and these films were exposed to light. Photocrosslinking reaction occurred in these cases also.

## Acknowledgement

Financial support from I.T.U. Research Fond is gratefully acknowledged.

## References

1. A. Reiser, *Photoreactive Polymers-The Science and Technology of Resists*, New York. 1989.
2. M. Kato and H. Kamagawa, *J. Polym. Sci., A-1*, **6**, 2993 (1968).
3. M. Kato and Y. Yoneshige, *J. Rad. Curing*, **7**, 23 (1980).
4. O. W. Webster, W. R. Hertler, D. Y. Sogah, W. B. Farnham and T. V. Rajanbabu, *J. Am. Chem. Soc.*, **105**, 5706 (1983).
5. A. Önen and Y. Yağcı, *Angew, Makromol. Chem.* **181**, 191 (1990).
6. S. P. Papas and R. A. Asmus, *J. Polym. Sci. Polym. Chem. Ed.*, **20**, 2643 (1982).