

# ***Polyfunctional Monomers as Additives for Enhancing the Radiation Copolymerization of Styrene with Polyethylene, Polypropylene, and PVC***

## **INTRODUCTION**

Additives which can increase the yield in the radiation grafting of monomers to polymers are useful, especially for radiation sensitive backbone materials, since in the presence of such additives lower total radiation doses are required to produce a particular percentage graft. Recently, mineral acid<sup>1-3</sup> has been successfully used for this purpose for a variety of radiation grafting systems. In the present communication, the use of polyfunctional monomers as additives ( $\approx 1\%$  v/v) are shown to enhance significantly the copolymerization yields of styrene in methanol to films of polyethylene and polypropylene under certain radiation conditions. The results obtained when the polyolefins are replaced by PVC as backbone polymer in these accelerated grafting reactions are also reported. Previously, polyfunctional monomers have been used to enhance the rates of radiation polymerization of monomers such as methyl methacrylate.<sup>4</sup> Thus the current results are not only of interest in a preparative context, but also support the concept that common intermediates exist in both radiation grafting and polymerization processes.

## **EXPERIMENTAL**

The following modification of previously reported<sup>1,2</sup> grafting procedures was adopted. Thus, in the actual grafting experiments, the polypropylene used was isotactic, doubly oriented film of thickness 0.06 mm ex-Shell Chemicals (Aust.) Pty. Ltd., whereas the polyethylene film was low density material of thickness 0.12 mm ex-Union Carbide. All grafting experiments were performed in quadruplicate in pyrex tubes (15  $\times$  2.5 cm) with styrene/methanol/additive solutions at  $20 \pm 1^\circ\text{C}$ . The backbone polymer films (4  $\times$  2.5 cm) were fully immersed in the monomer solutions, and the pyrex tubes were stoppered for irradiation, which was performed immediately after preparation in a 1200-Ci cobalt-60 source. At the completion of the reaction, the films were removed from solution, washed in an appropriate solvent, soxhlet extracted for 72 h, and then air-dried to constant weight.

## **RESULTS AND DISCUSSION**

Divinylbenzene (DVB) and trimethylolpropane triacrylate (TMPTA) were used as representative polyfunctional monomers for the enhancement effect. The data in Table I show that reactivities of both monomers are comparable in enhancing the grafting of styrene in methanol to polyethylene film in the 50–70% monomer concentration region. It is significant that this is the monomer concentration where the Trommsdorff peak<sup>1</sup> is observed and the grafted chains are longest.

When polypropylene is used as backbone polymer, the inclusion of DVB significantly enhances the radiation grafting of styrene in methanol at all monomer concentrations studied above 35% (Table II). Compared with grafting without additive, the presence of DVB also results in a shift in the position of the Trommsdorff peak to higher monomer concentration, suggesting that the additive polyfunctional monomer not only increases the grafting yield but also may change the structure of the grafted copolymer formed. At certain monomer concentrations (50%, 60%), the yield of graft copolymer is almost doubled by the addition of DVB.

The above polyolefin data contrast markedly with analogous results obtained when PVC is used as backbone polymer for the radiation grafting of styrene in methanol (Table III). Thus addition of DVB and TMPTA to the monomer solution accelerates the grafting reaction to PVC, but the magnitude of the enhancement in copolymer yield under the radiation conditions used is significantly lower than with the polyolefins. The results also suggest that the functionality of the monomer is of relevance in the PVC enhancement reaction.

Mechanistically, it is important to note that the presence of polyfunctional monomers in the grafting solution does not lead to a uniform enhancement in grafting. Instead, increased yields of

TABLE I  
Effect of Divinylbenzene and Trimethylolpropane Triacrylate on Grafting of Styrene in Methanol to Polyethylene Film<sup>a</sup>

Styrene (% v/v)	Graft (%)		
	No additive	DVB (1% v/v)	TMPTA (1% v/v)
20	14	15	—
30	37	41	39
40	75	74	73
50	109	136	137
60	89	121	—
70	89	—	105
80	68	74	59

<sup>a</sup> Dose rate of  $4.1 \times 10^4$  rad/h to total dose of  $2.4 \times 10^5$  rad.

TABLE II  
Effect of Divinylbenzene on Grafting of Styrene in Methanol to Polypropylene Film<sup>a</sup>

Styrene (% v/v)	Graft (%)	
	No additive	DVB (1% v/v)
20	37	38
30	132	92
35	101	144
40	75	132
50	58	111
60	56	101
70	41	—
80	35	55

<sup>a</sup> Dose rate of  $4.1 \times 10^4$  rad/h to total dose of  $2.4 \times 10^5$  rad.

TABLE III  
Effect of DVB and TMPTA on Radiation-Induced Grafting of Styrene in Methanol to Polyvinylchloride Film<sup>a</sup>

Styrene (% v/v)	Graft (%)		
	No additive	DVB (1%)	TMPTA (1%)
20	14.6	14.9	—
30	19.0	22.0	19.8
40	30.2	34.5	29.9
50	28.5	36.6	—
60	26.9	30.1	30.5
70	25.3	25.5	24.6

<sup>a</sup> Film (0.008 in.) irradiated at  $4.1 \times 10^4$  rad/h to  $2.5 \times 10^5$  rad in air.

copolymer are only observed at specific monomer concentrations. In the present experiments, the polyfunctional monomers appear to have a dual function, namely to enhance the copolymerization and also crosslink the grafted polystyrene chains. Such monomers have previously been used extensively to crosslink linear polymer chains. In the grafting experiments, branching of the growing grafted polystyrene chain occurs when one end of the polyfunctional monomer (e.g., DVB), immobilized during grafting, is bonded to the growing chain. The other end is unsaturated and free to initiate new chain growth via scavenging reactions. The new branched polystyrene chain may eventually terminate, crosslinked by reacting with another polystyrene chain or an immobilized divinylbenzene radical. Grafting is thus enhanced mainly through branching of the grafted polystyrene chain. Such a model for the enhancement reaction is consistent with the results obtained for PVC when compared with the polyolefins. Thus the lower enhancement in grafting yields ob-

served with PVC may reflect the role of radiolytically produced chlorine atoms from the PVC, leading to premature chain termination, especially for the branching process.

Possible changes in graft copolymer structure by the addition of these polyfunctional monomer additives are currently being investigated. The efficiency of these additives in enhancing radiation grafting yields is also being compared with the use of mineral acid, already reported for the same purpose.

We gratefully acknowledge support from the Australian Research Grants Committee and the Australian Institute of Nuclear Science and Engineering.

#### References

1. J. L. Garnett, *J. Rad. Phys. Chem.*, **14**, 79 (1979).
2. J. L. Garnett and N. T. Yen, *Aust. J. Chem.*, **32**, 585 (1979).
3. W. J. Chappas and J. Silverman, *J. Rad. Phys. Chem.*, **18**, 487 (1979).
4. M. M. Micko and L. Paszner, *J. Rad. Curing*, **7**(1), 6 (1980).

CHYE H. ANG  
JOHN L. GARNETT  
RONALD LEVOT  
MERVYN A. LONG

School of Chemistry  
The University of New South Wales  
Kensington, New South Wales 2033, Australia

Received March 5, 1982

Accepted July 22, 1982