

# NOTE

## Influence of Solvents on Radiation-Induced Graft Copolymerization of Acrylamide into Polyethylene Films

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### INTRODUCTION

The development of membranes for environmental protection has become a subject of great interest on a global basis. One of the most useful domains of membranes is the recovery and separation of dyes, chemicals, and toxic metal ions from the waste effluent.<sup>1,2</sup> The preparation of ion-exchange membranes by radiation-induced graft copolymerization of monomers into polymeric films has proved to be a very effective method.<sup>3–8</sup> The attractive feature of radiation grafting is that this process is virtually applicable to most of the polymer–monomer combinations without any consideration of the shape and the size of the material to be modified. Moreover, membranes with desired characteristics may be produced by proper control of the dose and dose rate of the radiation.<sup>9</sup>

The reaction conditions employed in a grafting reaction, such as monomer concentration, temperature, and additives, have considerable influence on the grafting kinetics. The use of solvents as additives in the reaction medium has been observed to be a major factor in governing the equilibrium degree of grafting.<sup>10–12</sup> Ang et al.<sup>11</sup> showed that methanol addition during the grafting of styrene into polypropylene shows an accelerative effect on the degree of grafting with a maxima at 70% methanol. Such behavior was found to be associated with the “Tromsdorff effect” arising in the system. In one of our studies<sup>13</sup> on the grafting of

methacrylic acid onto polypropylene fibers, it was observed that the grafting is considerably influenced by the nature of the solvent. The presence of a low level of methanol in the reaction medium was found to produce an accelerative effect on the degree of grafting but no grafting was observed when carried out in a pure methanol medium. It may therefore be stated that the interaction between the polymer matrix and the monomer–solvent mixture has a strong influence on the kinetics of graft copolymerization. By virtue of this, one may achieve a pronounced accelerative effect on grafting by using a proper solvent composition.<sup>14</sup>

Recently,<sup>15</sup> we reported the grafting of acrylamide into linear low-density polyethylene (LLDPE) films by a preirradiation method to produce membranes with a varying degree of grafting. Since the homopolymer formation is so intense, Mohr's salt was added to the grafting medium so as to inhibit the homopolymerization of acrylamide during the reaction. In the present work, the radiation grafting of acrylamide into LLDPE films was carried out in the presence of organic solvents. The influence of the nature of the solvent and their compositions vis-à-vis Mohr's salt on the degree of grafting was investigated.

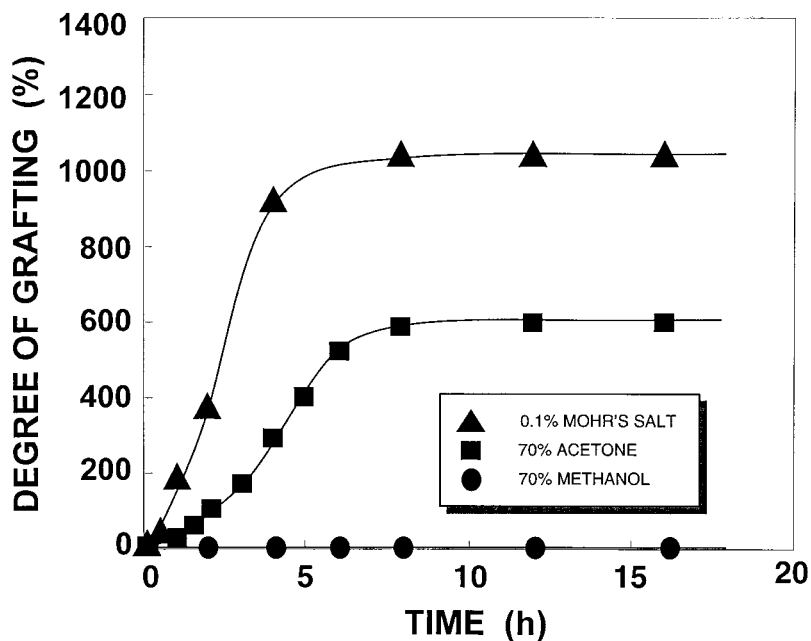
### EXPERIMENTAL

#### Materials

Polyethylene (PE) films of 40 microns thickness, processed from LLDPE chips (Grade F-19010, MFI 1.0), were supplied by Reliance Industries (India). The acrylamide monomer (SISCO India) was used as received without any purification. Acetone and methanol were

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**Figure 1** Variation of the degree of grafting with the time of reaction. Monomer concentration, 10%; preirradiation dose, 56 kGy; temperature, 60°C.

supplied by Merck (India) and were used as such.  $\text{FeSO}_4$  was used as the additive in the grafting medium and distilled water was used for all experiments.

#### Irradiation

The irradiation of PE films was carried out in air using a Co-60 gamma radiation source (900 curies). The dose rate of radiation was 0.36 kGy/h and the irradiation was carried out to a total dose of 56 kGy. The exposed films were stored at  $-4^\circ\text{C}$  before the grafting experiments.

#### Graft Copolymerization

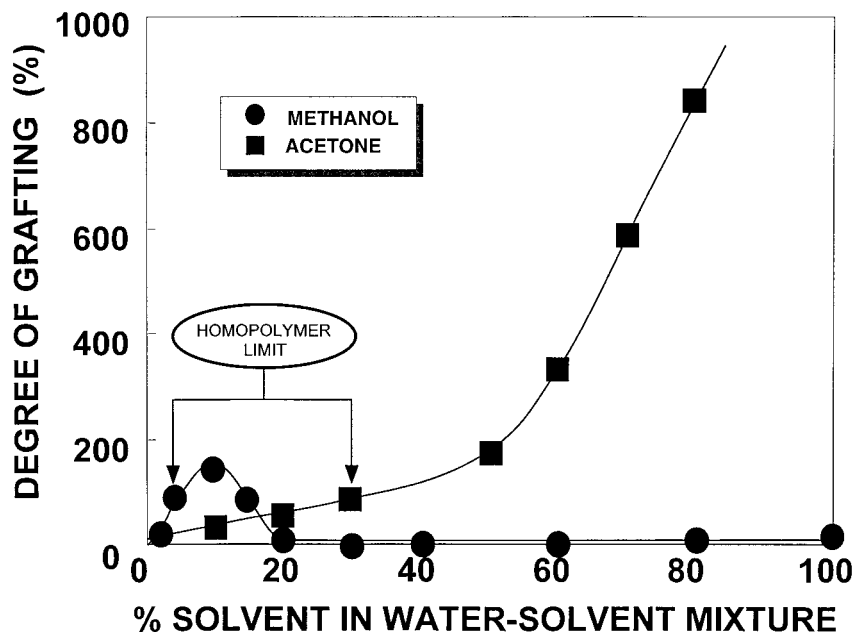
Graft copolymerization was carried out on irradiated PE films of size  $3 \times 3 \text{ cm}^2$  as reported earlier.<sup>15</sup> The PE film was placed in a glass tube containing a monomer solution of the desired composition. Nitrogen was purged into the glass tube to remove air from the grafting solution. A glass tube was placed in a water bath maintained at a constant temperature for a desired period. The grafted film was extracted with hot water to remove traces of any homopolymer adhering to the film surface. The grafted film was dried in an air oven at  $60^\circ\text{C}$  and weighed. The degree of grafting in the PE film was calculated from the following equation:

$$\text{Degree of grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100$$

where  $W_0$  and  $W_g$  are the weights of the ungrafted and grafted films, respectively.

#### RESULTS AND DISCUSSION

Extensive homopolymerization takes place at the very early stage of the grafting of acrylamide into PE films in aqueous medium, which leaves hardly any monomer for the grafting reaction.<sup>15</sup> As a matter of fact, we did not observe any grafting in the aqueous reaction medium. We observed that the Mohr's salt addition to the reaction medium leads to a homopolymer-free grafting reaction. The idea of the present investigation was to explore the possibility of using organic solvents besides Mohr's salt which may hinder the homopolymerization and, consequently, ensure a smooth grafting process. The influence of acetone and methanol as solvents in the grafting medium was studied and the results are presented in Figure 1. The acetone addition (70 vol %) to the reaction medium leads to a complete inhibition of homopolymerization and the grafting shows an increasing trend with increase in the reaction time, reaching saturation within 8 h. The trend in the grafting with acetone addition is quite similar to that of Mohr's salt (the plot for Mohr's salt is presented simply to have a qualitative view of the influence of the additive). On the other hand, in the presence of methanol (70%), both the grafting as well as homopolymerization did not take place under the present experimental conditions.



**Figure 2** Variation of the degree of grafting with the solvent composition. Monomer concentration, 10%; preirradiation dose, 56 kGy; temperature, 60°C; reaction time, 8 h.

The influence of the composition of the medium on the degree of grafting is presented in Figure 2. Interestingly, methanol shows a typical behavior where, initially, the grafting increases rapidly with increase in the methanol content, reaches a maximum, and thereafter decreases sharply. The maximum in the degree of grafting was observed at 10% methanol content. The grafting does not take place at all for the medium having a methanol content higher than 20%. A similar accelerative effect of methanol in the grafting of methyl methacrylate onto polypropylene films in benzene was reported by Burchill et al.<sup>14</sup> and a maximum of grafting was achieved at 10% methanol content. Acetone, on the other hand, shows a grafting trend different from that of the methanol addition. The onset of the Tromsdorff effect is visible here, where a sharp autoacceleration takes place at 30% solvent composition.

Methanol is known for the inhibitory action for the grafting of acrylic monomers into various polymers<sup>13</sup> and, as such, no grafting is reported in a medium comprising pure methanol. Our results concerning the PE-acrylic acid system are in agreement with these observations. The initial rapid increase in the grafting with the methanol content may be because, in the presence of methanol, the homopolymerization of acrylamide is considerably suppressed. No homopolymer formation was observed beyond 4% methanol content in the reaction mixture (Table I). At this stage, the viscosity of the grafting medium remains almost unchanged and the accessibility of the monomer to the grafting sites is maintained. Probably, the methanol content within the film is so low that it virtually has no inhibitory influ-

ence on the growth of the polyacrylamide chains.<sup>13</sup> Once the methanol content increases beyond 10%, perhaps the methanol content within the film increases and offers an inhibitory influence on the growth of the polyacrylamide chains as well.<sup>16</sup> This inhibitory effect is so pronounced that no grafting takes place beyond 20% methanol content in spite of the homopolymer-free reaction.

In the presence of acetone, no homopolymerization takes place beyond 30% solvent in the reaction medium (Table I). The monomer accessibility to the grafting sites within the film is maintained and the grafting proceeds smoothly. It may be stated that, like methanol, acetone also acts as the nonsolvent for polyacrylamide chains. Therefore, as soon as a polyacrylamide

**Table I** Influence of the Solvent Composition on the Homopolymer Yield

% Solvent	Percent Homopolymer	
	Methanol	Acetone
0	100	100
2	62	—
4	18	66
10	0	42
20	0	16
30	0	2
40	0	0

graft chain is formed, it precipitates out in the grafting medium. As a result, the termination of the growing chains by mutual recombination is considerably reduced and an acceleration in the grafting is observed. In an earlier investigation,<sup>16</sup> the authors mentioned that besides the Tromsdorff effect it is the contribution of base polymer swelling by the solvent which facilitates the monomer diffusion within the matrix and influences the grafting. In our system, the swelling of the polyethylene matrix in the reaction medium does not take place. It is the swelling of the grafted zone within the film which plays an important role. It is interesting to note that, unlike methanol, acetone shows no inhibitory action on the grafting within the film. It seems that the acetone content within the film is not enough to exert any inhibitory action against chain propagation. Probably, the methanol with its much higher solubility parameter ( $\delta = 14.5$ ) than that of acetone ( $\delta = 9.9$ ) may diffuse more within the hydrophilic polyacrylamide-grafted layer and exerts an inhibitory action beyond 20% solvent composition.<sup>17</sup>

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