

## 폴리프로필렌 필름에 Styrene과 2-Hydroxyethyl Methacrylate의 방사선 그래프트 공중합

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(1991년 10월 19일 접수)

### Radiation-Induced Graft Copolymerization of Styrene and 2-Hydroxyethyl Methacrylate onto Polypropylene Film

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(Received October 19, 1991)

**요약** : 스티렌이나 2-hydroxyethyl methacrylate(HEMA)를 단독 혹은 혼합하여  $\gamma$ -ray를 사용한 동시조사법으로 폴리프로필렌 필름에 그래프트 공중합시켰다. 스티렌과 2-hydroxyethylmethacrylate의 혼합조성비, 용매 형태 및 첨가제가 방사선그래프트율에 미치는 영향 및 반응성을 측정하였다. 단량체의 혼합조성비, 첨가제 및 용매가 폴리프로필렌 필름에 대한 그래프트율 뿐만 아니라 그래프트 공중합률 조성에 큰 영향을 끼쳤다. 단량체 혼합물에 첨가제로서 물을 사용하면 스티렌을 단독으로 사용한 경우를 제외한 모든 조성에서 그래프트율이 증가되었으며  $H_2SO_4$ 를 첨가하면 모든 조성에서 그래프트율이 향상되었다. 또한 다관능성 단량체는 스티렌 조성비가 큰 영역에서 효과적이었다.

**Abstract** : Graft polymerization of styrene and 2-hydroxyethylmethacrylate(HEMA), from both their binary and unitary systems, onto polypropylene film was investigated by means of the simultaneous  $\gamma$ -ray induced method. The influence of various factors such as styrene/HEMA feed ratio, solvent and additives on the grafting yield was studied. The reactivity ratios of the monomers in the binary system were also evaluated. The composition of the binary mixture, the presence of additives and solvent type were found to have strong influence on the total grafting yield and the composition of styrene and HEMA in the grafted polymer. The addition of water was effective to increase grafting yield at any feed ratio except single styrene, whereas  $H_2SO_4$  was effective to increase grafting values at any feed ratios of monomers. Multifunctional monomers were also very effective to increase grafting yield in high feed ratios of styrene.

## INTRODUCTION

Radiation-induced graft copolymerization is a well-known method for modification of the chemical and physical properties of polymeric materials, and is of particular interest for achieving specifically desired properties such as dyeability, blood compatibility, membrane quality and immobilization of bioactive materials.

Radiation conditions can be readily chosen to graft aromatic type monomers such as styrene especially when dissolved in a solvent like methanol, with little competing homopolymer formation.<sup>1</sup>

However when the technique is applied to radiation-sensitive monomers such as acrylic acid, methacrylic acid, polyfunctional acrylates and their esters, homopolymer is formed more rapidly than grafted copolymer. One of the methods for minimizing the problem is the addition of metal salts such as  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  to the grafting solution.<sup>2,3</sup> However, by this metal ion technique, both grafting and homopolymerization are suppressed, with homopolymerization being suppressed to a greater extent. Thus it permits reasonable grafting yield with little homopolymer contamination.

It has recently been found that if a comonomer technique is used for grafting the radiation sensitive monomers, and if styrene is one of the monomers in the mixture, the copolymerization can be achieved by the simultaneous irradiation method with little homopolymer formation.<sup>4,5</sup> Mixed monomers can also be used in grafting onto polymers to introduce dual properties such as hydrophilicity and hydrophobicity.<sup>6</sup> In this study, the graft polymerization of styrene and HEMA, from both their unitary and binary systems, onto polypropylene film was investigated by the simultaneous  $\gamma$ -ray induced method to increase grafting yield of monomers to backbone polymer as well as to introduce dual properties such as hydrophilicity and hydrophobicity.

## EXPERIMENTAL

### Materials

Polypropylene films (0.12 mm thickness) were provided by Union Carbide, styrene by Monsanto (Australia) Ltd., HEMA from Fluka AG and methanol from BDH chemicals, Australia Pty., Ltd.

Monomers were purified by column chromatography on alumina, a procedure that has previously been satisfactory for radiation copolymerization.<sup>7</sup> The other chemicals were AR grade and used without further purification.

### Irradiation Procedure

Grafting experiments were performed in Pyrex tubes, solvent being added first, followed by monomers to a total volume of 20 ml. Polypropylene films (30 mm  $\times$  50 mm) were then fully immersed in the solutions of monomers. After irradiation using Co-60 source at the Australian Nuclear Science and Technology Organization, the grafted polymer film was quickly removed from the monomer solution, extracted in benzene, then methanol for 72 hrs to remove homopolymer, followed by drying in air to remove most of the solvent and then in a ventilated oven at 50°C to constant weight. The percent of grafting was calculated as follows.

$$\frac{(W_g - W_i)}{W_i} \times 100$$

where  $W_i$  and  $W_g$  represent the weights of the initial and grafted films respectively.

The composition of the polypropylene film grafted with a mixture of the two monomers was determined by IR spectrometer using a calibration curve, which was made at 1600  $\text{cm}^{-1}$  for polypropylene films grafted with styrene alone.

## RESULTS AND DISCUSSION

The data for the effect of concentration of styrene and HEMA on grafting yield are reported in Table 1. It was found that the grafting yield of styrene increased with increasing concentration of

**Table 1.** Grafting Percent of Styrene and HEMA onto Polypropylene in the Presence of Methanol<sup>a</sup>

Monomer Concentration(V/V)	Graft Percent	
	Styrene	HEMA
20	8.1	0
30	18	0
40	50	15
50	43	40
60	29.2	solid

<sup>a</sup>Dose rate : 0.052 Mrad/hr

Total dose : 0.2 Mrad

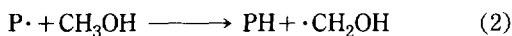
monomer up to the Trommsdorff peak, i. e. 40% styrene in methanol and then decreased. On the other hand, HEMA was grafted only in the 40% and 50% monomer concentrations, and solidified in more than 60% concentrations.

These data show that HEMA can be grafted to polypropylene film but only in a limited range of monomer concentration.

The results in Table 2 illustrate the influence of the variation of methanol/H<sub>2</sub>O composition on the grafting on HEMA at 30% monomer concentration.

These results clearly indicate that HEMA does not graft in the absence of water. However the addition of a small quantity of water was accompanied by a slight increase in graft. When 17.5 v/v % water was added to the monomer solution, the grafting yield reached a maximum value, however with 35% water, the grafting solution was solidified after irradiation.

The results of Table 1 and 2 may be explained by the following mechanisms.



where P $\cdot$  represents a radical of the backbone polymer formed in this grafting system, M denotes monomer. When reaction (1) proceeds, grafting occurs, whereas with reaction (2), the backbone polymer radical abstracts H atoms from the methanol leading to  $\cdot CH_2OH$  radicals which produces

**Table 2.** Effect of Methanol/H<sub>2</sub>O Composition on Grafting of HEMA onto Polypropylene<sup>a</sup>

HEMA Concentration (V/V)	Solvent Composition(V/V)		Graft Percent
	MeOH	H <sub>2</sub> O	
30	70	0	0
30	66.5	3.5	2
30	63	7	18.4
30	59.5	10.5	30
30	56	14	27.4
30	52.5	17.5	30.5
30	49	21	21.4
30	35	35	solid

<sup>a</sup>Dose rate : 0.052 Mrad/hr

Total dose : 0.2 Mrad

homopolymer rather than graft.

In the case of styrene, the reaction (1) is faster. If HEMA is added to the monomer solution, grafting by the reaction (1) is slow, and reaction (2) predominates. The addition of water to the HEMA grafting system may retard reaction (2), leading to grafting even at low monomer concentrations.

Mixtures of styrene and HEMA at various compositions in the presence of methanol were used for grafting to polypropylene films. The results are shown in Table 3 by calculating grafting yields versus comonomer concentration in methanol for various comonomer compositions. The total grafting yield increased with increasing composition of styrene and the concentration of comonomers. As the composition of styrene increased, styrene fractions in the grafted copolymer increased appreciably with nearly infinite values of HEMA.

The result in Table 4 showed the effect of water on radiation grafting yields with respect to various styrene/HEMA compositions. The addition of water to HEMA/styrene mixtures or HEMA alone increased the total grafting yield. By contrast, water in the styrene-methanol grafting solution had a detrimental effect on the grafting yield of styrene.

#### Grafting in the Presence of Polyfunctional Monomers

The result in Table 5 shows the effect of polyfu-

**Table 3.** Effect of Concentration and Feed Ratio of Monomers on Grafting onto Polypropylene Using Methanol<sup>a</sup>

Feed Ratio		Graft Percent		
Volume St : HEMA	Mole St : HEMA	Monomers Concentration 20% (V/V)	Monomers Concentration 40% (V/V)	Monomers Concentration 60% (V/V)
0 : 5	0 : 1	0	15	—
1 : 4	0.21 : 0.79	5.5(1.2 <sup>b</sup> /4.3 <sup>c</sup> )	12.1(2.8/9.3)	20.6(4.5/16.1)
2 : 3	0.41 : 0.59	6.2(2.2/4)	12.8(5.2/7.6)	40.4(14.5/25.9)
2.5 : 2.5	0.51 : 0.49	7 (3/4)	14.3(7.5/6.8)	38.4(18.2/20)
3 : 2	0.61 : 0.39	7.3(4/3.3)	19.4(11.8/7.6)	45.8(25/20.8)
4 : 1	0.81 : 0.19	8.2(5.7/2.5)	37.5(27.8/9.7)	53.5(33.6/19.9)
5 : 0	1 : 0	8.1	50	29.2

<sup>a</sup>Dose rate : 0.052 Mrad/hr, Total dose : 0.2 Mrad<sup>b</sup>Graft percent of styrene in copolymer, <sup>c</sup>Graft percent of HEMA in copolymer**Table 4.** Effect of H<sub>2</sub>O in Methanol on Grafting of Styrene/HEMA to Polypropylene<sup>a</sup>

Feed Ratio		Graft Percent		
Volume St : HEMA	Mole St : HEMA	Pure MeOH	MeOH/H <sub>2</sub> O : 95/5(V/V)	MeOH/H <sub>2</sub> O : 90/10(V/V)
0 : 5	0 : 1	15	15.1	17.4
1 : 4	0.21 : 0.79	12.1(2.8 <sup>b</sup> /9.3 <sup>c</sup> )	13.8(3.8/10)	13.6(4.6/9)
2 : 3	0.41 : 0.59	12.8(5.2/7.6)	20.4(11.1/9.3)	32.5(16.6/15.9)
2.5 : 2.5	0.51 : 0.49	14.3(7.5/6.8)	26 (16.4/9.6)	49.3(31/18.3)
3 : 2	0.61 : 0.39	19.4(11.8/7.6)	38 (23.5/14.5)	76.5(52.5/24)
4 : 1	0.81 : 0.19	37.5(27.8/9.7)	63.3(54/9.3)	42.8(40/2.8)
5 : 0	1 : 0	50	34.5	20.4

<sup>a</sup>Dose rate : 0.052 Mrad, Total dose : 0.2 Mrad, Total monomers concentration : 40 V/V %<sup>b</sup>Grafting percent of styrene in copolymer, <sup>c</sup>Graft percent of HEMA in copolymer**Table 5.** Effect of Polyfunctional Monomers on Grafting of Styrene/HEMA onto Polypropylene Using Methanol<sup>a</sup>

Feed Ratio		Graft Percent		
Volume St : HEMA	Mole St : HEMA	Control	TMPTA <sup>b</sup>	DGDMA <sup>c</sup>
0 : 5	0 : 1	15	7	7.7
1 : 4	0.21 : 0.79	12.1(2.8 <sup>d</sup> /9.3 <sup>e</sup> )	7.7(2/5.7)	10 (2.5/7.5)
2 : 3	0.41 : 0.59	12.8(5.2/7.6)	12.7(5.8/6.9)	13 (5.6/7.4)
2.5 : 2.5	0.51 : 0.49	14.3(7.5/6.8)	15.2(8/7.2)	15 (8/7)
3 : 2	0.61 : 0.39	19.4(11.8/7.6)	23 (13.6/9.4)	19.2(12.2/7)
4 : 1	0.81 : 0.19	37.5(27.8/9.7)	49 (34.5/14.5)	38.8(28.4/10.4)
5 : 0	1 : 0	50	88.4	72

<sup>a</sup>Dose rate : 0.052 Mrad/hr, Total dose : 0.2 Mrad, Total monomers concentration : 40 V/V %<sup>b</sup>TMPTA : Trimethylol propane triacrylate(1% V/V), <sup>c</sup>DGDMA : Diethyleneglycol dimethacrylate(1% V/V),<sup>d</sup>Graft percent of styrene in copolymer, <sup>e</sup>Graft percent of HEMA in copolymer

nctional monomers such as TMPTA and DGDMA on grafting yield with respect to various comonomer compositions. In these results, polyfunctional monomers accelerated the grafting yield at high styrene compositions in the binary mixtures, but decelerated the grafting yield at high HEMA compositions.

Large grafting yields can be obtained if the free radical yield of polymer is higher than that of monomer. It is known that the free radical yield of polypropylene  $G(P\cdot)$  under irradiation is higher than that of styrene  $G(St\cdot)$ , whereas the free radical yield of HEMA  $G(HM\cdot)$  is very high compared with that of polypropylene. Addition of polyfunctional monomer can thus accelerate the homopolymerization of HEMA to give low grafting yields of HEMA.

In the presence of a polyfunctional monomer such as TMPTA, branching of the grafted polymer can occur. Branching of the growing grafted polymer chain occurs when one end of the polyfunctional monomer, immobilized during grafting, is bonded to the growing chain. The other end(or ends) is unsaturated and free to initiate a new chain length via scavenging reactions. The new branched polymer(polystyrene) chains may eventually terminate, crosslinked by reacting with another nearby polymer(polystyrene) chain or immobilized polyfunctional radical. Grafting is thus increased mainly through the branching of the grafted poly-

mer chain.

#### Acid Enhancement Effect in Grafting

The data in Table 6 show the effect of  $H_2SO_4$  addition on grafting yields for various comonomer compositions. In these results,  $H_2SO_4$  is particularly effective to increase grafting yield at any compositions in the binary mixture.

The mechanism of acid enhancement in radiation grafting is complicated by the variety of chemical constituents present in any grafting systems.<sup>5,9-11</sup> Solvents are particularly relevant since these materials which wet and swell the backbone polymer generally enhance grafting.<sup>12</sup> In earlier work, the acid enhancement was attributed to two predominant factors, that is, (i) the radiolytic yield of hydrogen atoms and (ii) the extent to which grafting monomer(polystyrene) was solubilized in bulk solution. Solvent structure was also considered to be important since those solvents with high radiolytic yields of hydrogen atoms such as methanol were efficient reagent for grafting. It was proposed that the radiolytically produced hydrogen atoms(equations 3, 4) abstracted hydrogen atoms from trunk polymer(PH) yielding additional grafting sites.

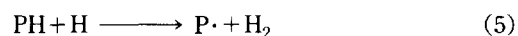
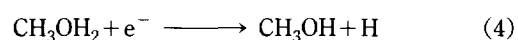
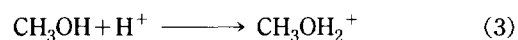


Table 6. Effect of  $H_2SO_4$  on Grafting of Styrene/HEMA onto Polypropylene Using Methanol<sup>a</sup>

Feed Ratio		Graft Percent	
Volume St : HEMA	Mole St : HEMA	Control	$H_2SO_4(0.2 M)$
0 : 5	0 : 1	15	22
1 : 4	0.21 : 0.79	12.1(2.8 <sup>b</sup> /9.3 <sup>c</sup> )	15.4(3.5/11.9)
2 : 3	0.41 : 0.59	12.8(5.2/7.6)	22 (9.7/12.3)
2.5 : 2.5	0.51 : 0.49	14.3(7.5/6.8)	24.8(13.2/11.6)
3 : 2	0.61 : 0.39	19.4(11.8/7.6)	30.5(17.7/12.8)
4 : 1	0.81 : 0.19	37.5(27.8/9.7)	52.8(31/21.8)
5 : 0	1 : 0	50	66

<sup>a</sup>Dose rate : 0.052 Mrad, Total dose : 0.2 Mrad, Total monomers concentration : 40 V/V %

<sup>b</sup>Grafting percent of styrene in copolymer, <sup>c</sup>Grafting percent of HEMA in copolymer

The above radiation chemistry mechanism for grafting enhancement<sup>5,13,14</sup> fails to explain a number of recently reported further observations including (i) enhancement only for certain acid and monomer concentration, (ii) the acid enhancement in sensitized photografting where radiation chemistry effects are not relevant.

Mechanistically one of the most important observations concerning the acid effect is the recent detailed systematic study of the swelling of polyethylene in the presence of methanolic solutions of styrene which indicates that partitioning of non-polar monomer into non-polar substrates may be significantly improved by the inclusion of mineral acid in the grafting solution.<sup>15</sup>

This partitioning behavior may be interpreted as an example of the salting out technique employed in solvent extraction. In the present grafting systems, the driving force for the increased partitioning of monomer into the substrate is the reduced solubility of styrene in the bulk solution due to the presence of dissolved electrolyte. The net result of this driving force is higher rate of monomer diffusion into, and equilibrium monomer concentration within, the substrate.

The higher concentration of monomer at grafting site favours propagation of growing chains. The increased partitioning of monomer occurs in the graft region of the backbone polymer when acid is dissolved in the bulk grafting solution. This

permits higher concentrations of monomer to be available for grafting at a particular backbone site in the presence of these additives. It is thus the effect of these ionic species on partitioning which is essentially responsible for the observed increase in radiation grafting yield in the presence of acid. Radiolytically generated free radicals can also be expected to make some contribution to this effect in the system where initiation occurs by ionizing radiation, however such a contribution would be relatively small.

### Reactivity Ratios

The data in Table 7 show the effect of solvent on grafting of comonomers with respect to various compositions of styrene and HEMA. Compared with methanol, the reactivity of HEMA in tetrahydrofuran (THF) was much larger than that of styrene in the binary mixture.

Graft copolymerization of styrene ( $M_1$ ) and HEMA ( $M_2$ ) was investigated in a radiation-induced grafting system. The effect of various factors such as styrene/HEMA feed ratio, solvent and additives on reactivity ratios was evaluated (Table 8). Reactivity ratios under different grafting conditions were calculated from experimental data using the Fineman-Ross method.<sup>16</sup>

$$\frac{F}{f}(f-1) = r_1 \frac{F^2}{f} - r_2 \quad (6)$$

where  $F = M_1/M_2$ ,  $f = m_1/m_2$ ,  $M_1$  and  $M_2$  refer to

**Table 7.** Effect of Solvents on Grafting of Styrene/HEMA to Polypropylene<sup>a</sup>

Feed Ratio		Graft Percent	
Volume St : HEMA	Mole St : HEMA	MeOH	THF
0 : 5	0 : 1	15	—
1 : 4	0.21 : 0.79	12.1(2.8 <sup>b</sup> /9.3 <sup>c</sup> )	224 (3/221)
2 : 3	0.41 : 0.59	12.8(5.2/7.6)	59 (5.7/53.3)
2.5 : 2.5	0.51 : 0.49	14.3(7.5/6.8)	35.5(6/29.5)
3 : 2	0.61 : 0.39	19.4(11.8/7.6)	20 (4.5/15.5)
4 : 1	0.81 : 0.19	37.5(27.8/9.7)	7.5(3.2/4.3)
5 : 0	1 : 0	50	5.3

<sup>a</sup>Dose rate : 0.052 Mrad, Total dose : 0.2 Mrad, Total monomers concentration : 40 V/V %

<sup>b</sup>Grafting percent of styrene in copolymer, <sup>c</sup>Grafting percent of HEMA in copolymer

the compositions of styrene and HEMA in the feed respectively, and  $m_1$  and  $m_2$  to the compositions of styrene and HEMA in polymer respectively. The influence of concentration of monomers on reactivity ratios in the presence of methanol was investigated and shown in Fig. 1. The reactivity values found at 20% and 60% monomer concentration were almost identical to those published by Niwa<sup>17</sup> ( $r_1=0.45$ ,  $r_2=0.54$ ). Different values, however, were found in the 40% monomer concentration. The reactivity ratio of  $r_1$  for the 40% monomer concentration was greater than that found for either the 20% or 60% monomer solutions. This behaviour can be attributed to Trommsdorff effect, caused by styrene i. e. at the 40% monomer concentration. When additives such as TMPTA, DGDMA and  $H_2SO_4$  were added to the grafting system at 40% monomer concentration, the effect of those additives on reactivity ratios was not great. However, when  $H_2O$  was incorporated into the monomer solution, the reactivity ratio  $r_1$  in this system was found to be higher than that without additives, leading to a reduced  $r_2$  (Table 8 and Fig. 2).

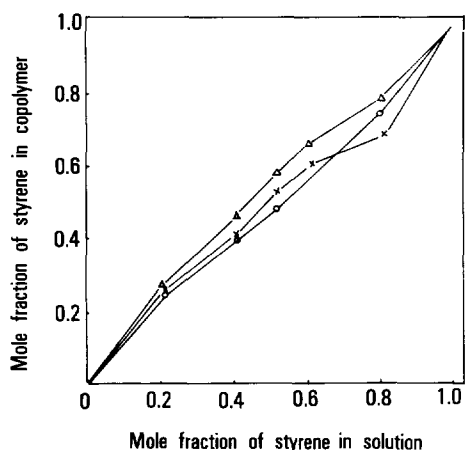


Fig. 1. Effect of monomer composition in solution on monomer composition in copolymer. Grafting conditions : dose rate 0.052 Mrad/hr, total dose 0.2 Mrad : (○) 20% monomers concentration, (△) 40% monomers concentration, (×) 60% monomers concentration.

The reactivity ratio in THF was significantly different to that in methanol. The results from Fig. 2 indicate that the reactivity ratio  $r_2$  in THF was much larger than that in MeOH, a result which is of significant value in preparative work, especially when synthesizing HEMA copolymers of polyethy-

Table 8. Monomer Reactivity Ratio for Styrene( $M_1$ ) and HEMA( $M_2$ ) Grafting

Grafting Condition	$r_1$	$r_2$
Total monomers concentration 20%	0.45	0.75
Total monomers concentration 40%	1.33	0.65
Total monomers concentration 60%	0.45	0.56
Total monomers concentration 40% + TMPTA	0.82	0.4
Total monomers concentration 40% + DGDMA	1.33	0.65
Total monomers concentration 40% + $H_2SO_4$	0.7	0.39
Total monomers concentration 40% + $H_2O$ 5%	0.98	0.25
Total monomers concentration 40% + $H_2O$ 10%	1.42	0.31
Total monomers concentration 40% + THF	0.58	6.0

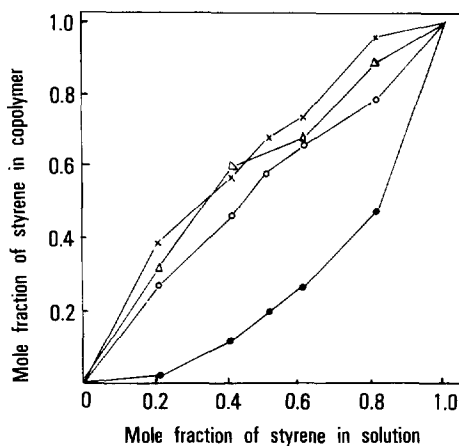


Fig. 2. Effect of monomer composition in solution on monomer composition in copolymer. Grafting conditions : dose rate : 0.052 Mrad/hr, total dose 0.2 Mrad : (○) pure MeOH, (△) MeOH/ $H_2O$  : 95/5, (×) MeOH/ $H_2O$  : 90/10, (●) THF.

lene. The data demonstrate the conditions for achieving not only high grafting yields of HEMA but also copolymer which contains HEMA almost exclusively with virtually no styrene.

### CONCLUSIONS

The main conclusions to be drawn from the above experiment are as follows.

Monomer concentration, the composition of binary mixture, the presence of additives and solvent type were found to have strong influence on the total grafting yield and the composition of styrene and HEMA in the grafted polymer.

The grafting yield of styrene increased with increasing concentration of monomer up to the Trommsdorff peak, i. e. 40% styrene in methanol and then decreased. On the other hand, HEMA was grafted only in the 40 and 50% monomer concentrations, and solidified in more than 60% monomer concentrations.

The addition of water was effective to increase grafting yield at any feed ratio except single styrene, whereas  $H_2SO_4$  was effective to increase the total grafting values at any feed ratios of monomers.

Polyfunctional monomers accelerated the grafting yield at high styrene compositions in binary mixtures, but decelerated the grafting yield at high HEMA compositions.

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