

# Ultraviolet Curable Dry Polymer Films from Emulsion Polymers

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**ABSTRACT:** Low levels of functional acrylic monomers were incorporated into a core-shell acrylic copolymer by seeded emulsion polymerization. The increase in glass transition temperature,  $T_g$ , from DSC measurement has showed that although certain amount of crosslinking reactions have occurred during the polymerization and isolation of the copolymer, the dried copolymer films could undergo further curing by UV irradiation. The structure and amount of the functional monomer, concentration of photoinitiator, and the extent of UV exposure have exerted significant influence on the  $T_g$  of the dry copolymer films. Because of the rela-

tively low level of incorporated unsaturation, there was no significant change in FTIR during the curing of the film. Further, crosslinking of the copolymer film induced by UV irradiation has significantly increased the resistance to swelling in alkaline solution, although the gel content remained the same. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2317–2322, 2006

**Key words:** UV-curable; second-stage curing; dry film; emulsion polymer; functional monomer

## INTRODUCTION

UV curable polymers have found increasing applications in coating, adhesive, and ink industries because of their solvent free characteristics, versatility, low energy requirements, and low temperature operation. A common commercial UV-curing formulation prepared for coating application usually consist of one or more acrylated oligomers or prepolymers and at least one multifunctional acrylate monomer.<sup>1,2</sup> Under intense illumination, reactive free radicals can be generated in high concentrations by photolysis of an initiator, and thus, promote the polymerization of monomers and oligomers.<sup>3</sup> Although acrylates display good weathering resistance, they also have some disadvantages such as health hazards and inhibition of polymerization by atmospheric oxygen.<sup>3</sup>

Although most of the photosensitive systems used in today's UV curing applications consist of liquid resins, a dry film technology may present some advantages for specific end-uses. Dry photosensitive plates can be stored for months in the dark and can be processed in the presence of air. However, there is also a drawback of operating in a solid medium, which is the sharply reduced rate of polymerization that results from severe mobility restrictions of the reactive sites in the solid medium.<sup>2,4</sup>

In the present study, low levels of functional acrylic monomers were incorporated into a core-shell acrylic copolymer by seeded emulsion polymerization. The copolymer latex incorporated with photoinitiator was dried before UV irradiation. Physical properties of the copolymer films were examined by differential scanning calorimetry (DSC) and fourier transform infrared spectroscopy (FTIR). Other properties such as resistance to swelling and gel content of the copolymer film were also investigated.

## EXPERIMENTAL

### Materials

Butyl acrylate (BA, >99%, Fluka, Switzerland), methyl methacrylate (MMA, >99%, BDH), styrene (St, >99%, R and M), 2-hydroxyethyl methacrylate (HEMA, 97%, Aldrich), ethyl methacrylate (EMA, >99%, TCI), methacrylic acid (MAA, >99%, Merck-Schuchardt), and acrylic acid (AA, >99%, Fluka) were used without further purification. Technical-grade isobornyl acrylate (IBA), isobornyl methacrylate (IBMA), tripropylene glycol diacrylate (TPGDA), 1,6-hexanediol diacrylate (HDDA, 90%), and pentaerythritol triacrylate (PETA) were purchased from Aldrich (Germany) and used as supplied, as the functional monomers. Potassium persulfate (97%) supplied by Avocado Research Chemicals was used as the polymerization initiator. The polymerization emulsifiers were sodium lauryl sulfate and NP-40, which is nonylphenol polyethoxy- late with an average of 40 ethylene oxides per mole- cule.

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TABLE I  
Formulations (in grams) of Polymer 1 and Polymer 2

Ingredient	Polymer	
	1	2
Distilled water	560.0	490.0
NP40 <sup>a</sup>	0.7	3.2
Sodium lauryl sulfate	3.5	3.5
Potassium persulfate	1.2	1.0
Seedlatex (Polymer 1)	—	87.5
Styrene	—	55.1
Methyl methacrylate (MMA)	35.0	3.7
Butyl acrylate (BA)	84.0	53.9
Methacrylic acid (MAA)	21.0	2.5
Acrylic acid (AA)	—	1.2
2-hydroxyethyl methacrylate (HEMA)	—	3.0
Ethyl methacrylate (EMA)	—	2.7
Total charge	705.4	707.3

<sup>a</sup> Nonyl phenol ethoxylate (40 units of ethylene oxide).

### Preparation of emulsion samples

The emulsion polymerization was carried out in a glass reactor, with the stirrer speed controlled between 200 and 500 rpm. The mode of emulsion polymerization was a semicontinuous process and was carried out at 75°C.

The seed latex was prepared according to the formulation of Polymer 1, while the core-shell polymer was prepared by seeded emulsion polymerization according to the formulation of Polymer 2 in Table I. The core-shell polymer, thus prepared, was to serve as control in this study. Subsequently, ethyl methacrylate in Polymer 2 was replaced with similar molar quantity of a functional monomer in each modification to make the UV-curable materials.

### Preparation of copolymer film

The latex, incorporated with 0.052–0.467 mmole of photoinitiator/g copolymer, was drawn on aluminum foil or glass panel with a bar coater of 50- $\mu$ m wet film thickness. The wet film was dried at reduced pressure in a vacuum oven at room temperature for 3 h, followed by exposure to UV light generated by a 400-W mercury lamp at wavelengths between 315 and 380 nm for the specified time.

### Fourier transform infrared spectroscopy

Infrared spectra of the polymer films were recorded on a Perkin–Elmer Spectrum 1000 Fourier Transform Spectrometer.

### Glass transition temperature

Differential Scanning Calorimetry (Perkin–Elmer 7 Series Thermal Analysis System) was used to determine

the glass transition temperature ( $T_g$ ) of each copolymer film. To erase any thermal history of the polymer and also to ensure a greater proportion of amorphous region so that a more pronounced  $T_g$  could be obtained, the sample was first scanned from  $-55$  to  $200^\circ\text{C}$ . It was then quenched rapidly at  $-50^\circ\text{C}/\text{min}$  to  $-55^\circ\text{C}$ . The next heating scan was carried out from  $-55$  to  $150^\circ\text{C}$  at  $20^\circ\text{C}/\text{min}$ . Each sample was between 10 and 20 mg, encapsulated in nonvolatile aluminum sample pan.

### Swelling of copolymer film

The dried film that was coated on aluminum foil was cut into round shape with a disc cutter of fixed diameter of 20.4 mm ( $d_0$ ). The film was then soaked in 0.25M sodium hydroxide solution at room temperature for 30 h. The diameter of the swollen film was measured ( $d_1$ ). The swelling is assumed to occur to the same extent in all directions. Percent of swelling of film in volume was estimated as  $\approx [(d_1/d_0)^3 - 1] \times 100\%$

### Gel content

Accurately weighed sample was extracted in a Soxhlet extractor with toluene for 12 h. The insoluble fraction was dried in a vacuum oven at  $60^\circ\text{C}$  overnight, cooled down in a desiccator, and the weight determined.

## RESULTS AND DISCUSSION

### The influence of type and amount of functional monomer on polymer $T_g$

In this study, the functional acrylate used was 0.175 mmol/g copolymer, which amounted to 2.3 mol % of the total molar amount of the monomer mixture used in the second stage polymerization, unless specified otherwise. When EMA was replaced with each of the functional monomers listed in Table II, the  $T_g$  of the copolymer has generally increased, except for IBA. This has shown that certain degree of crosslinking has

TABLE II  
The Influence of Incorporation of Different Functional Monomer (0.175 mmol/g Polymer)

Functional monomer incorporated	$T_g$ ( $^\circ\text{C}$ )
EMA (control)	18.4
IBA	17.4
IBMA	20.6
2HEMA	19.4
TPGDA	20.4
HDDA	24.0
PETA	24.6

**TABLE III**  
The Influence of the Amount of IBA, IBMA, and PETA

Functional monomer	Concentration of functional monomer (mmol/g)	$T_g$ (°C)
IBA	0.175	17.4
ISA	0.525	22.2
IBMA	0.175	20.6
IBMA	0.525	25.5
PETA	0.175	24.6
PETA	0.525	44.1

occurred during the emulsion polymerization and the subsequent isolation of the copolymer film.

Among the diacrylate monomers, HDDA has produced more significant change in  $T_g$  than has TPGDA. The increase in  $T_g$  was the highest for the copolymer incorporated with PETA because of the presence of three acrylate double bonds in PETA molecule.

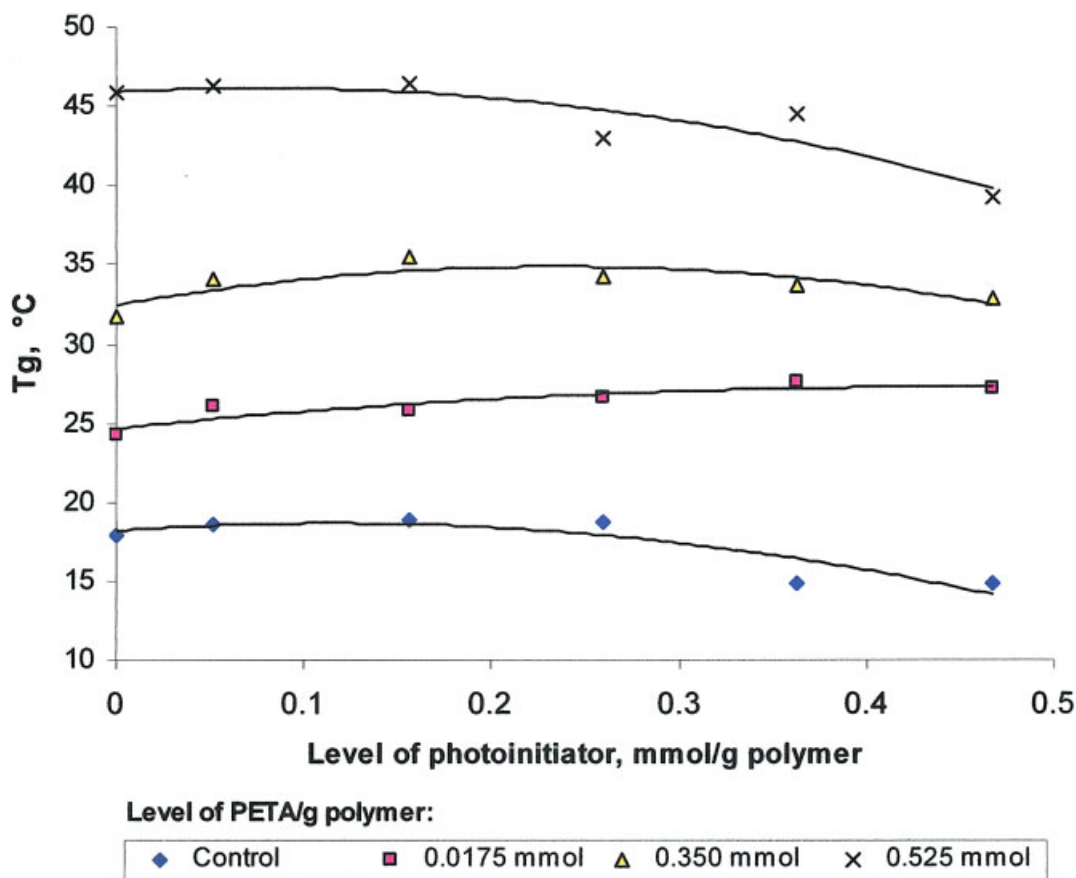
Results in Table III show that higher amount of functional monomers in the copolymer system could also lead to higher  $T_g$ , presumably due to the occurrence of higher level of effective crosslinking between different polymer chains.

#### Amount of photoinitiator and UV exposure time on polymer $T_g$

Selli et al. have reported that when photopolymerization was carried out in the presence of increasing amounts of photoinitiator, the overall radical concentration has increased correspondingly.<sup>5,6</sup> A maximum radical concentration was reached with 1 mol % of photoinitiator, while higher concentrations became less effective, due to radical-radical encounters,<sup>5</sup> which could give rise to various other secondary reactions.

Since PETA has caused the largest increase in  $T_g$ , it was studied separately by incorporating various amount of PETA into the copolymer and UV-cured at different level of photoinitiator. Figure 1, shows that higher amount of PETA in the copolymer has led to higher  $T_g$ . There was, however, little variation in the polymer  $T_g$  with increasing amount of photoinitiator. In the control polymer, the increase of the photoinitiator concentration has produced polymer with lower  $T_g$ .

Dry polymer films with 0.175 mmole of PETA and EMA (control) per gram of polymer were exposed to



**Figure 1** The influence of the amount of photoinitiator on the  $T_g$  of copolymer with different amounts of PETA. Each polymer film has been irradiated with UV light for 30 s. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE IV**  
The Influence of Photoinitiator on UV Exposure<sup>a</sup>

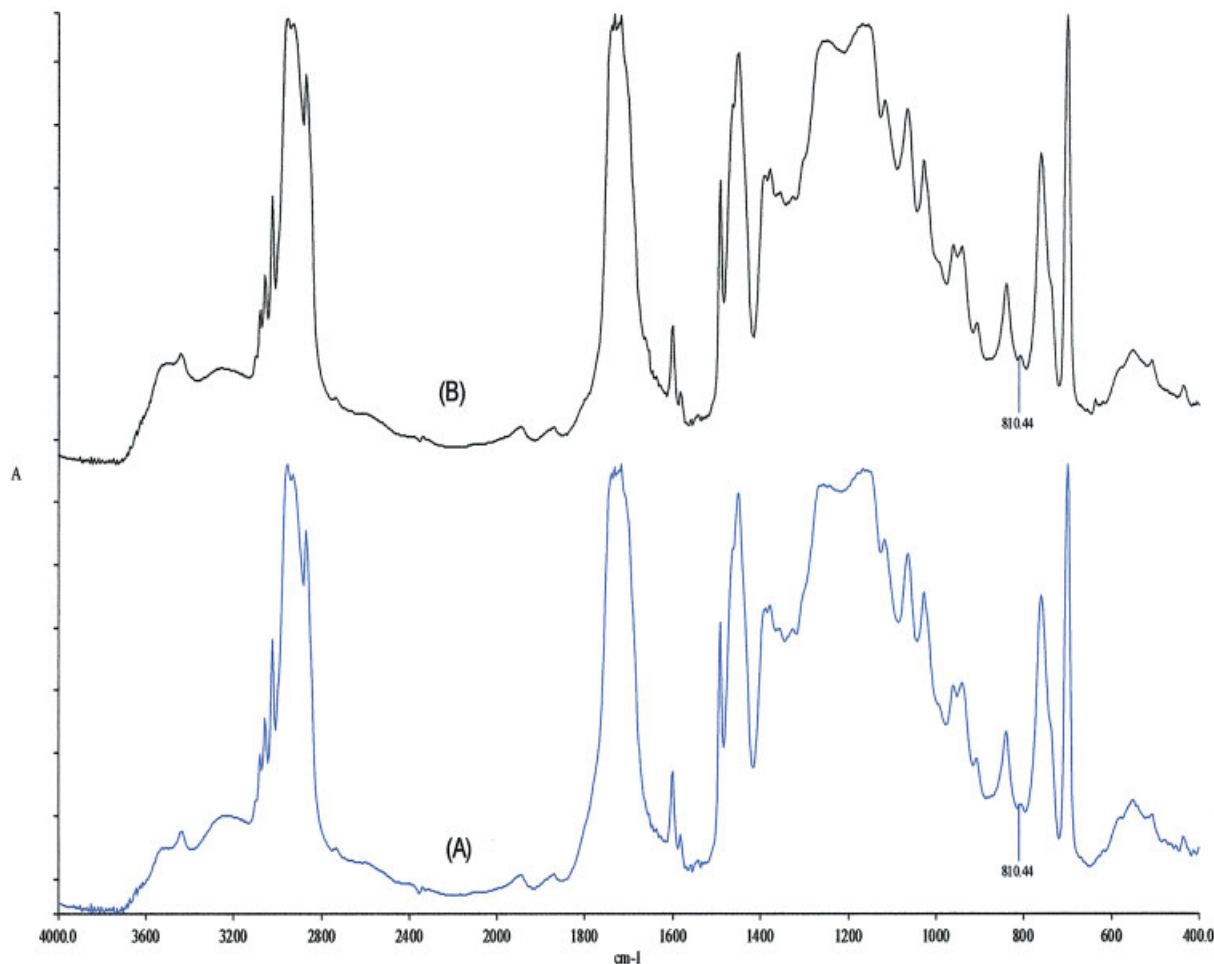
UV irradiation time (s)	T (°C)		EMA
	With photoinitiator	Without photoinitiator	
0	26.6	24.5	12.0
30	26.0	26.3	12.5
150	27.4	27.5	14.6
300	29.0	29.4	14.6
600	30.0	29.6	14.9

<sup>a</sup> The copolymer with EMA was the control.

UV irradiation for 0, 30, 150, 300, and 600 s, respectively. Results in Table IV show that there was no significant change in the  $T_g$  of the UV irradiated film containing PETA with or without the presence of photoinitiator. This could be due to the high reactivity of PETA, which could readily crosslink without the aid of the photoinitiator. There was no further increase in  $T_g$  after the first 300 s of UV exposure. This is presumably due to the depletion of the

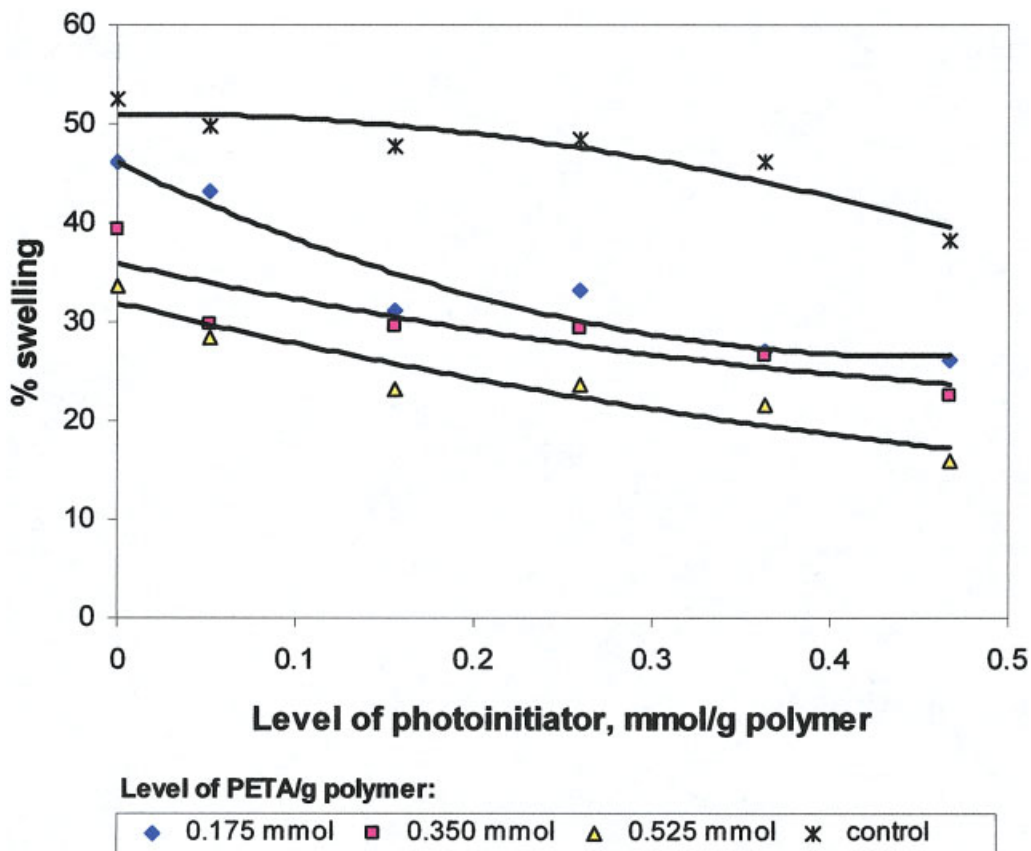
acrylic double bonds and the gel effect caused by segmental mobility restrictions upon prolonged UV exposure<sup>2,4,7-9</sup>.

FTIR has been used in the analysis of C=C unsaturation of the UV irradiated polymer films<sup>8,10-14</sup>, where the decrease of the absorbance peak at 810  $\text{cm}^{-1}$  was attributed to the involvement of C=C in the crosslinking reactions. In the case of PETA incorporated copolymer (Fig. 2), the FTIR spectra of the same film before and after the UV-irradiation appeared identical, presumable at 2.3 mol % level, the weak peak of the C=C double bonds could not be used for accurate determination. The absorbance at 810  $\text{cm}^{-1}$  has only changed from 0.43 to 0.41 after the UV irradiation. It is not totally surprising because the copolymer film was dried before UV-irradiation; hence, the mobility of the polymer network was much restricted. Besides, the  $T_g$  measurements (Table II) have shown that significant crosslinking by the incorporated functional monomer has already occurred during the polymerization and isolation of the copolymer film.



**Figure 2** FTIR spectra of the polymer incorporated with PETA: (A) before and (B) after the UV-irradiation. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]





**Figure 3** The influence of the amount of PETA and photoinitiator on the swelling of polymer film. Each polymer film has been subjected to 30 s of UV irradiation. The control sample is without functional monomer. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### Swelling of copolymer film in alkaline solution

The control sample without any functional monomer was found to swell readily in 0.25M NaOH solution after soaking for 30 h, with an increase of 55% in volume. Incorporation of the same molar amount of different functional monomer has led to lower swelling to 34–51% under the same conditions. The largest reduction of swelling was observed for copolymer incorporated with PETA. The extent of swelling is being used as a measure of the amounts of crosslink between copolymer chains and the crosslink density in the same copolymer structure.

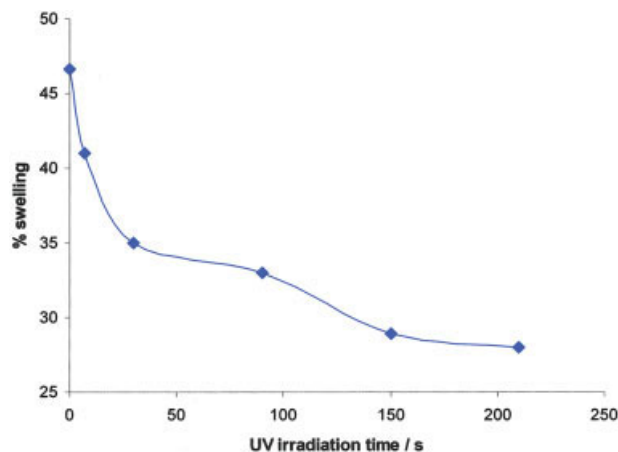
### The influence of the amount of functional monomer and photoinitiator

Figure 3 showed that when the level of incorporated PETA was increased from 0.175 to 0.525 mmol/g copolymer, the extent of swelling in alkaline solution has decreased. Further, drastic decrease in swelling was observed when the copolymer film was treated with higher level of photoinitiator and subjected to 30 s of UV-irradiation. The observation can be explained as follows: The initial crosslinking, presumably occurred

between different copolymer chains, has led to drastic increase in molecular weight and chain entanglements resulting in more restricted chain mobility. This would result in an initial decrease in swelling in the alkaline solution. Subsequent crosslinking promoted by UV irradiation in the presence of photoinitiator could have occurred more within the same copolymer chain, which did not increase the molecular weight, but producing higher crosslink density within the same structure, and consequently becoming more resistant to swelling in the alkaline solution.

### UV exposure time on the extent of swelling of the polymer film

Similar to the influence of increasing the amounts of functional monomer and photoinitiator, longer exposure to UV irradiation has reduced the extent of swelling of the polymer film in alkaline solution (Fig. 4). The effect of further crosslinking was more clearly seen in the swelling results than those on the polymer  $T_g$  (Table IV). With about 90 s of UV exposure, further crosslinking in the polymer film has effectively reduced the swelling of the film to the same extent as when triple the amount of PETA was incorporated.



**Figure 4** The influence of UV exposure time on the copolymer film with PETA (0.175 mmol/g polymer) in the presence of photoinitiator (0.052 mmol/g polymer). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### Gel content determination

Table V shows that the unexposed control sample has 22.3% of insoluble copolymer after toluene extraction. Upon UV irradiation (30 s) in the presence of photoinitiator (0.052 mmol/g copolymer), the gel content of the control sample has gone up to 47.4%. This indicated that a UV induced crosslinking has occurred, which has increased the gel content by 25.1%.

For the other copolymers incorporated with 0.175 mmol/g polymer of difunctional or trifunctional monomer, the initial gel content was already around 94% and has not changed significantly after the UV irradiation. The high initial gel content was consistent to the occurrence of crosslinking during the emulsion

**TABLE V**  
Gel Content of the Copolymer Films Incorporated with 0.175 mmol/g Functional Monomer and the Influence of UV Exposure on the Copolymer Films Containing 0.052 mmol/g of Photoinitiator

Functional monomer incorporated into the polymer	Gel content (%)	
	Unexposed, without photoinitiator	UV exposed, with photoinitiator
EMA (control)	22.3	47.4
HDDA	94.2	97.5
TPGDA	93.6	92.8
PETA	93.8	91.8

polymerization and the subsequent casting and drying of the copolymer films. UV exposure of these already crosslinked polymers did not further increase the gel content of the polymers. The further crosslinking was shown by the reduction of swelling in alkali solution.

### CONCLUSIONS

Low levels of functional acrylic monomers were incorporated into a core acrylic copolymer, by seeded emulsion polymerization. The increase in  $T_g$  from DSC measurement has showed that although certain amount of crosslinking reactions have occurred during emulsion polymerization, the dry polymer films could undergo second-stage curing by UV irradiation. The structure and amount of the functional monomer, concentration of photoinitiator, and the extent of UV exposure have exerted significant influence on the glass transition temperature and the resistance to swelling of the dry copolymer film in alkaline solution. The presence of photoinitiator was found to induce more crosslinking in the UV curing process, presumably producing higher crosslink density in the same copolymer chain as there was no increase in the gel content of the cured film.

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