

# Synthesis and Characterization of Methacrylic acid-based Copolymers

HORNG-JER TAI<sup>1</sup>, PANG-CHI CHIANG<sup>2</sup>

*Institute of Biotechnology and Chemical engineering, I-Shou University*

**Abstract**—*In this study, 1-hydroxycyclohexyl phenyl ketone (HCPK) was used as a photoinitiator, methacrylic acid (MAA), 2-(dimethylamino)ethyl methacrylate (DMAEMA), and trimethylol-propane trimethacrylate (TMPTMA) were copolymerized by UV polymerization to prepare transparent and flat copolymer films with different monomer ratios. Surface energy was measured using a contact angle meter. We found that the addition of TMPTMA reduced the surface energy of the copolymer films. The water content test also confirmed that the addition of TMPTMA inhibited water absorption. In the dynamic mechanical test, the higher the MAA content, the higher the glass transition temperature (T<sub>g</sub>) of the copolymer film, and the addition of TMPTMA also slightly increased the T<sub>g</sub>.*

**Indexed Terms**—*Methacrylic Acid, Photoinitiator, Surface Energy, Glass Transition Temperature*

## I. INTRODUCTION

With the advancement of information technology, the applications of displays have become more diverse. The substrate of flat-panel displays is mainly glass. However, the heavy and fragile nature of glass itself does not meet the requirements for light and portable modern displays and flexible displays have become a new research and development direction. Flexible displays are thin, soft, and easy to carry, and will be an indispensable product for future entertainment. The development of flexible substrate materials will affect the mass production process of future flexible displays, and if production of the new substrates can be modified or adjusted with existing equipment, it will greatly attract the willingness of glass substrate manufacturers to invest. The polymer polymerized by the monomer DMAEMA is highly transparent but easily soluble in water and has a low glass transition temperature. It had been copolymerized with furfuryl methacrylate to help dispersing carbon nanotubes onto

a flexible polyethylene terephthalate substrate to fabricate transparent conductive films [1]. We added MAA with a high glass transition temperature, hoping to improve the mechanical strength of the material without affecting its transparency. The copolymer poly (MAA-DMAEMA) had been developed as a synthetic polyampholyte for cryopreservation of cells [2]. In order to apply the polymer film as the display substrate, it is necessary to further improve its water resistance and mechanical strength. TMPTMA, which is multifunctional and hydrophobic, is added to reduce the hydrophilicity of the polymer film. TMPTMA is one of the most effective crosslinking agents. Polymers modified with TMPTMA have excellent weather resistance, chemical resistance, water resistance and wear resistance. TMPTMA can easily form cross-links with linear methacrylate polymers [3]. UV polymerization has the advantage of being able to achieve a high reaction rate at room temperature. Therefore, we used HCPK as a photoinitiator to copolymerize MAA, DMAEMA and TMPTMA to synthesize films with high transparency and high glass transition temperature for replacing the glass substrate of traditional displays.

## II. EXPERIMENTALS

### A. Materials

Methacrylic acid (MAA, 99%, Sigma-Aldrich), 2-(dimethylamino) ethyl methacrylate, (DMAEMA, reagent grade, Fujifilm Wako Chemicals), trimethylolpropane trimethacrylate (TMPTMA, technical grade, Sigma-Aldrich), 1-hydroxycyclohexyl phenyl ketone (HCPK, 99%, Sigma-Aldrich) were purchased and used as received.

### B. Sample Preparation

Mixtures of MAA and DMAEMA in three molar ratios (80:20, 50:50, 20:80) were prepared. 0.5 phr (0.5 parts per hundred parts by weight of MAA-DMAEMA mixture) of HCPK was added to the mixtures,

respectively, and stirred evenly by a magnetic stirrer at 25 °C. Caution must be taken to prevent the mixtures from exposure to light during this process. A simple mold consisting of three layers of polypropylene (PP) film with a pre-cut rectangular cavity in the middle layer was used. The two bottom PP layers were glued with double-sided tape and fixed on a steel plate also with double-sided tape. The mixtures were then poured into the PP mold, and then covered with the upper layer of PP film. An extra glass plate was placed on top of the PP mold to prevent its deformation. The poly (MAA-co-DMAEMA) films were obtained by irradiating with a UV lamp with a power of 12 mW/cm<sup>2</sup> for 30 min. For the poly (MAA-co-DMAEMA-co-TMPTMA) films, an additional 5 phr (5 parts per hundred parts by weight of MAA-DMAEMA mixture) of TMPTMA was added. The preparation procedure was the same as that for poly (MAA-co-DMAEMA) films.

### C. Characterization and Testing

A Hitachi U-3300 UV-Vis absorption spectrophotometer was employed to measure the transparency of the films. The absorbance of light was measured as a function of the wavelength in the range of 350–750 nm at a scan rate of 300 nm/min. The surface property was characterized using a Dataphysics OCA20 automatic contact angle measuring and contour analysis system. The values of water uptake were obtained by measuring the weight gain after placing pre-dried samples in a programmable temperature and humidity chamber at 100% humidity and 40 °C for 3 h. The values of glass transition temperature (T<sub>g</sub>) were measured using a TA-Instruments DMA 2980 in 3-point bending mode, at a frequency of 1 Hz and a ramp rate of 3 °C/min. T<sub>g</sub> was determined by the peak of the loss tangent.

## III. RESULTS AND DISCUSSION

### A. Film Transparency

If a polymer film is to be used as a display substrate, its transparency is the most important consideration. The following equation describes the exponential decay of monochromatic light as it travels through a film

$$I = I_0 \exp(-\beta l) \quad (1)$$

, where  $I$  and  $I_0$  are the intensities of the incident and transmitted light, respectively,  $l$  is the film thickness,  $\beta$  is the absorption coefficient. Materials with lower

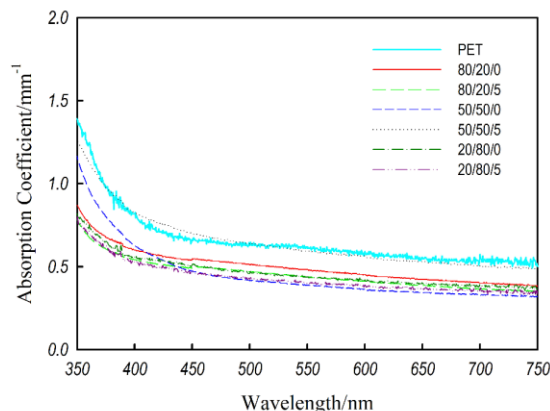


Figure 1. Absorption coefficients for various copolymer films. The numbers in the legends are the ratios of MAA/DMAEMA/TMPTMA

absorption coefficients will have better transparency. We used commercially available PET film as a reference material and compared the experimentally obtained absorption coefficients with each other. Since MAA and DMAEMA have good compatibility, there will be no phase separation during the polymerization reaction, so the transparency of DMAEMA itself will not be reduced. It can be seen from Figure 1 that the absorption coefficients of the poly(MAA-co-DMAEMA) and poly(MAA-co-DMAEMA-co-TMPTMA) films synthesized with different monomer ratios are not much different, and are generally lower than that of the PET film, which indicates that the transparency of the synthesized polymer films is better than that of PET.

### B. Water Absorption

In terms of water absorption, since both MAA and DMAEMA are water-soluble, the synthesized poly(MAA-co-DMAEMA) films are supposed to be highly hygroscopic at room temperature. Figure 2 is a comparison of saturated water absorption of the poly(MAA-co-DMAEMA) and poly(MAA-co-DMAEMA-co-TMPTMA) films at 40°C and 100% humidity for 3 h. It can be seen that after adding TMPTMA, the water content will decrease. This is because TMPTMA itself is hydrophobic, and it will cause cross-linking reaction of polymer chains to form a network structure. The movement of molecular chains is restricted in a cross-linked network, and water molecules are not easy to enter the interior of the

material. MAA will form hydrogen bonds with water molecules, and its affinity with water is higher than that of DMAEMA, but it forms a polymer PMAA with a higher Tg, which causes the movement of polymer

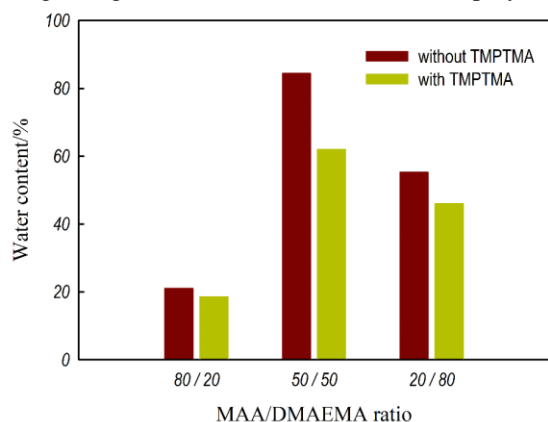


Figure 2. Water content for various copolymers films.

chains highly restricted and consequently leads to a lower degree of water absorption. In contrast, DMAEMA is relatively hydrophobic, but it forms a polymer PDMAEMA with a low Tg. Therefore, the water absorption property of the copolymers is controlled by the two factors: the interaction between glass transition temperature and water affinity. The results showed that the copolymer with a MAA/DMAEMA ratio of 50/50, which had an intermediate Tg and water affinity, had the highest water absorption. And the copolymers with a MAA/DMAEMA ratio of 80/20, more hydrophilic but with a higher Tg, has a lower water absorption than the copolymer with a MAA/DMAEMA ratio of 80/20.

### C. Surface Energy

The surface energy of a solid can be determined by measuring the contact angle using a pendant drop method. The relation between the surface energy of solid  $\sigma_s$ , the surface energy of liquid  $\sigma_l$  and the solid-liquid interfacial energy  $\sigma_{sl}$  can be described by the Young equation

$$\cos\theta_\infty = \frac{\sigma_s - \sigma_{sl}}{\sigma_l} \quad (2)$$

, where  $\theta_\infty$  is the measured contact angle. Usually the surface energy of the test liquid,  $\sigma_l$ , is known. In this study, we used glycerol, which has a surface energy of 63 dyne/cm, as the test liquid. And according to Berthelot [4],

$$\sigma_{sl} = \sigma_s + \sigma_l - 2\sqrt{\sigma_s \sigma_l} \quad (3)$$

By combining (2) and (3),

Table 1. Comparison of surface energy values for the synthesized films (unit : dynes/cm)

MAA/DMAEMA	Without TMPTMA	With TMPTMA
100/0	18.7±2.37	18.4±1.72
80/20	29.5±1.35	26.8±2.01
50/50	27.4±1.68	20.9±1.69
20/80	34.0±1.67	33.5±0.34
0/100	33.9±1.30	31.5±1.43

$$\cos\theta_\infty = 1 - 2\sqrt{\frac{\sigma_s}{\sigma_l}} \quad (4)$$

Using (4), the surface energy  $\sigma_s$  can be calculated with the measured contact angle. It was found that the contact angles of the poly(MAA-co-DMAEMA-co-TMPTMA) films were larger than those of the corresponding poly(MAA-co-DMAEMA) films in the pendant drop experiment. The calculated surface energy values are listed in Table 1. It can be seen that the addition of the nonpolar TMPTMA monomer will reduce the surface energy of the copolymer films.

### D. Glass Transition Temperature

In the dynamic mechanical analysis spectrum of a polymer, the storage modulus will be higher at low temperature, while the loss modulus will be lower. As the temperature increases, the segmental movement of the polymer chain will gradually intensify, the storage modulus will decrease, and the loss modulus will increase, so that  $\tan \delta$  (the ratio of loss modulus to storage modulus) will increase accordingly. The temperature at which  $\tan \delta$  reaches a maximum is generally defined as the glass transition temperature. Because the Tg of the polymer formed from MAA is higher than that of the polymer formed from DMAEMA, the Tg of the copolymer will increase with

increasing MAA/DMAEMA ratio. It can be seen

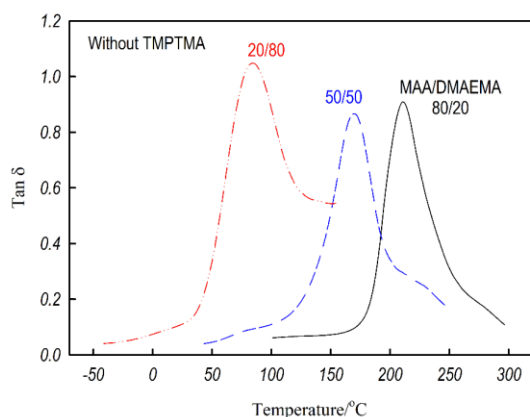


Figure 3. DMA tan  $\delta$  values for poly(MAA-co-DMAEMA) films.

from Figure 3 for poly (MAA-co-DMAEMA) that the Tg is only 84°C when the ratio of MAA/DMAEMA is 20/80, and the Tg increases to 210°C when the ratio of MAA/DMAEMA is 80/20. From Figure 4, it is clear that with the addition of TMPTMA, the Tg also increases from 113°C for the ratio of MAA/DMAEMA of 20/80 to 215°C for the ratio of 80/20. With or without TMPTMA, the higher the MAA content, the higher the Tg. Comparing Figures 3 and 4, we can also investigate the effect of adding TMPTMA on Tg. When the MAA/DMAEMA ratio is 20/80, the Tgs of the copolymers with and without TMPTMA are 113°C and 84°C, respectively. When the ratio is 50/50, they are 181°C and 167°C, respectively, and when the ratio is 80/20, they are 215°C and 210°C, respectively. The Tg of the copolymer with the same MAA/DMAEMA ratio increases when TMPTMA is added. This is because TMPTMA will cause the copolymer to undergo a cross-linking reaction to produce a network structure. The cross-links hinder the segmental motion and the Tg increases. From the above Tg values, it is also found that the increasing effect of TMPTMA on Tg decreases with increasing MAA/DMAEMA ratio. That is, the increasing effect of TMPTMA is less pronounced for the poly (MAA-co-DMAEMA-co-TMPTMA) with a higher Tg.

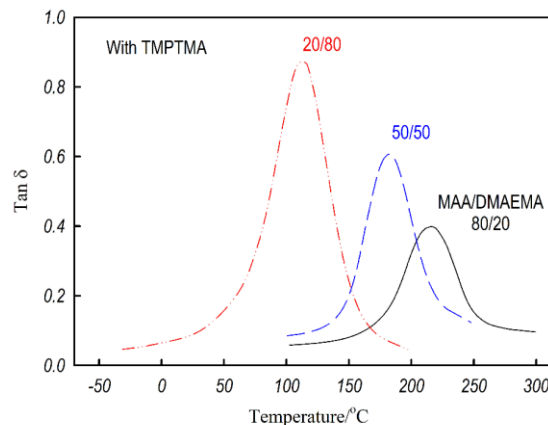


Figure 4. DMA tan  $\delta$  values for poly(MAA-co-DMAEMA-co-TMPTMA) films.

## REFERENCES

- [1] T. Lee, B. Kim, S. Kim, J. H. Han, H. B. Jeon, Y. S. Lee, and H. Paik, -Fabrication of flexible, transparent and conductive films from single-walled carbon nanotubes with high aspect ratio using poly ((furfuryl methacrylate)-co-(2-(dimethylamino) ethyl methacrylate)) as a new polymeric dispersant, *Nanoscale*, vol. 7, pp. 6745-6753, 2015.
- [2] R. Rajan and K. Matsumura, -Preparation of Novel Synthetic Cryoprotectants, *Cryobiology and Cryotechnology*, vol. 60, no. 2, pp. 99-103, 2014.
- [3] S M. Lomakin, J.E. Brown, R. S. Breese, and M. R. Nyden, -Investigation of the thermal stability and char-forming tendency of cross-linked poly (methyl methacrylate), *Polym. Degrad. Stab.*, vol. 41, pp. 229-243, 1993.
- [4] L. A. Girifalco and R. J. Good, -A theory for the estimation of surface and interfacial energies. I. Derivation and application to interfacial tension, *J. Phys. Chem.*, vol. 61, no. 7, pp. 904-909, 1957.