

Article

## Transparent Heat-Resistant PMMA Copolymers for Packing Light-Emitting Diode Materials

Shu-Ling Yeh <sup>1,2</sup>, Chao-Yuan Zhu<sup>1,\*</sup> and Shiao-Wei Kuo<sup>3,4,\*</sup>

<sup>1</sup> Department of Applied Chemistry, National Chiao Tung University, Hsinchu, 300, Taiwan; E-Mail: ShuLingYeh@itri.org.tw

<sup>2</sup> Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu 300, Taiwan

<sup>3</sup> Department of Materials and Optoelectronic Science, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan

<sup>4</sup> School of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

\* Authors to whom correspondence should be addressed; E-Mails: cyzhu@mail.nctu.edu.tw (C.-Y.Z.); kuosw@faculty.nsysu.edu.tw (S.-W.K.); Tel.: +886-3571-2121 (ext. 56582) (C.-Y.Z.); +886-752-52000 (ext. 4079) (S.-W.K.); Fax: +886-752-54099 (S.-W.K.).

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**Abstract:** Transparent and heat-resistant poly(methyl methacrylate) copolymers were synthesized by bulk polymerizing methyl methacrylate (MMA), isobornyl methacrylate (IBMA), and methacrylamide (MAA) monomers. Copolymerization was performed using a chain transfer agent to investigate the molecular weight changes of these copolymers, which exhibited advantages including a low molecular weight distribution, excellent optical properties, high transparency, high glass transition temperature, low moisture absorption, and pellets that can be readily mass produced by using extrusion or jet injection for packing light-emitting diode materials.

**Keywords:** poly(methyl methacrylate); optical polymers; thermal resistance; packing LED

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## 1. Introduction

The key transparent polymers for optical and photonic applications include poly(methyl methacrylate) (PMMA), polycarbonate, polystyrene, and cyclic olefin copolymers. However, these polymers have shortcomings, such as yellowing or high cost. Polymers exhibiting heat resistance and low moisture absorption are attractive in the thermoplastic and optoelectronic industries [1–3], particularly for use in light guide sheets and light-emitting diode (LED) module materials. Heat-resistant and low-moisture polymers provide thermal and structural stability. However, the applicability of these thermoplastic polymers is limited by their heat resistance and moisture absorption during polymerization. PMMA is a widely used transparent polymer, also known as organic glass [4], exhibiting strong climate resistance [5,6], chemical resistance, ease of mass production, and low cost. Although PMMA has many advantages, certain disadvantages require improvement, including its temperature resistance and moisture absorption properties, which limit its applications. To increase its glass transition temperature, PMMA can be mixed using an extrusion screw or synthesized from free radical copolymerization with various monomers [7–9]. Enhancing heat resistance might reduce the transparent nature of PMMA, thereby restricting its applications [10–14]; thus, it is essential to increase the heat-resistant properties of PMMA while maintaining excellent transparency, which has been widely discussed in our previous studies [15–21].

In this study, we developed a novel acrylic material exhibiting heat resistance and low moisture absorption using a bulk copolymerization synthesis process and combining bulky acrylate with methyl methacrylate (MMA) monomers. The monomer composing the bulky structure of the copolymers exhibited three characteristics: (1) a strong ring structure or nanoparticle to enhance the glass transition temperature ( $T_g$ ) of the PMMA copolymers [22–26]; (2) reduced moisture absorption because of the hydrophobic properties of the PMMA copolymer [27,28]; and (3) avoidance of poor transmittance in the near UV region (250–380 nm) as a result of the aromatic ring in the structure. Therefore, a series of random poly(methyl methacrylate-*co*-isobornyl methacrylate) (PMMA-*co*-PIBMA) copolymers and poly(methyl methacrylate-*co*-methacrylamide-*co*-isobornyl methacrylate) (PMMA-*co*-PMAA-*co*-PIBMA) were synthesized by using bulk polymerization in this study. We analyzed the thermal properties of these copolymers by using a differential scanning calorimeter (DSC) and a thermogravimetric analyzer (TGA), determining their molecular weights by using gel permeation chromatography (GPC). Finally, we obtained optimized copolymers based on PMMA that exhibited a high glass transition temperature and were suitable for use in injection molding for packing light-emitting diode applications.

## 2. Experimental Section

### 2.1. Materials

Methyl methacrylate (MMA, 99%, SHOWA, Tokyo, Japan) was distilled from finely ground  $\text{CaH}_2$  prior to use. The bulky monomer of isobornyl methyl methacrylate and methacrylamide was purchased from Evonik Degussa Corporation, Taipei, Taiwan. Benzoyl peroxide (BPO, initiator) was purchased from Evonik, and *N*-dodecyl mercaptan (NDM; chain transfer agent) was obtained from Sigma-Aldrich, (St. Louis, MO, USA).

## 2.2. Synthesis of PMMA-co-PIBMA and PMMA-co-PMAA-co-PIBMA Copolymer

The bulk copolymerization of MMA, isobornyl methacrylate (IBMA), or methacrylamide (MAA) was conducted in a beaker. The initiator BPO was added at a proportion of 1.5 wt% of the monomer. The monomer and initiator were mixed at low temperatures. After the mixture was dispersed, it was placed over a water bath at 80 °C for 30 min for pre-polymerization until the viscosity increased. All experiments were conducted in atmospheric conditions. The resultant polymers were heated in an oven at 120 °C for 3 h to remove the unreacted monomer and initiator and maintain the stability of the polymers. The molecular weights of the obtained copolymers were adjusted by adding mercaptan as a chain transfer agent.

## 2.3. Characterization

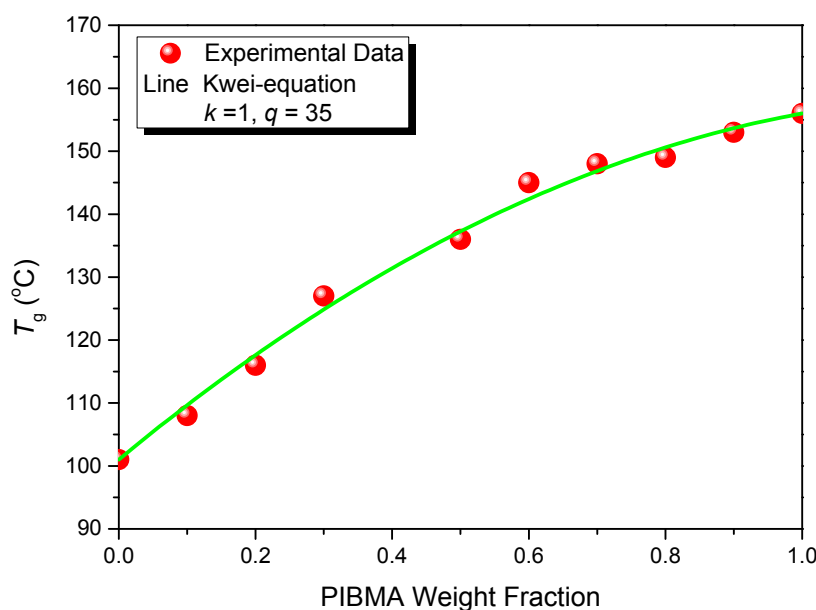
Molecular weights and molecular weight distributions were determined through gel permeation chromatography (GPC) using a Waters 510 high-performance liquid chromatograph (Waters, Taipei, Taiwan) equipped with a 410 differential refractometer and three Ultrastyrigel columns (100, 500, and 1000 Å) connected in series, with tetrahydrofuran as the eluent (flow rate: 1.0 mL/min). DSC was performed using a TA-Q20 instrument (Waters, Taipei, Taiwan) operated at a scan rate of 20 °C/min over a temperature range from 0 to 250 °C under a N<sub>2</sub> atmosphere.

## 3. Results and Discussion

Poly(methyl methacrylate-co-methacrylamide) (PMMA-co-PMAA) has been widely discussed in our previous study. A large positive deviation in the behaviour of  $T_g$  based on the Kwei equation from DSC analyses indicates that strong hydrogen bonding exists between these two monomer segments. In this study, we first pay attention to the PMMA-co-PIBMA copolymers that were synthesized using bulk polymerization; the reaction conditions and molecular weights are summarized in Table 1. Polymerization was performed over a low-temperature water bath to avoid heat aggregation. The reaction produced a high-yield transparent polymer. GPC analyses of the PMMA-co-PIBMA copolymers revealed that the polydispersity index was quite narrow, being in the range of 1.20–1.28. The molecular weights of the PMMA-co-PIBMA copolymers were in the range of  $3.5 \times 10^5$  to  $4.2 \times 10^5$ , being too high to be used in the jet injection process. The low-molecular-weight PMMA-co-PIBMA copolymer was obtained using mercaptan as a transfer agent, through bulk copolymerization over a low-temperature water bath (40 °C). The amount of bulky bonding monomer affected the thermal properties of the copolymers. The bulky-structure monomer IBMA was added in amounts of 10 wt% to 100 wt% for bulk copolymerization. After the reaction, the liquid monomer turned into a solid, and DSC analysis was performed to determine the glass transition temperature of these copolymers. Figure 1 shows the  $T_g$  profiles of the copolymer fabricated using the one-stage method. The glass transition temperatures of the PMMA-co-PIBMA copolymers increased as the amount of the IBMA monomer increased. When the amount of the IBMA monomer in the mixture was increased up to *ca.* 50 wt%, the glass transition temperature rapidly elevated from 100 °C to *ca.* 150 °C; further increases in the amount of this bulky monomer resulted in a slight increase in the glass transition temperature. In general, the Kwei Equation [29] predicted the glass transition temperature of the random copolymer by the following:

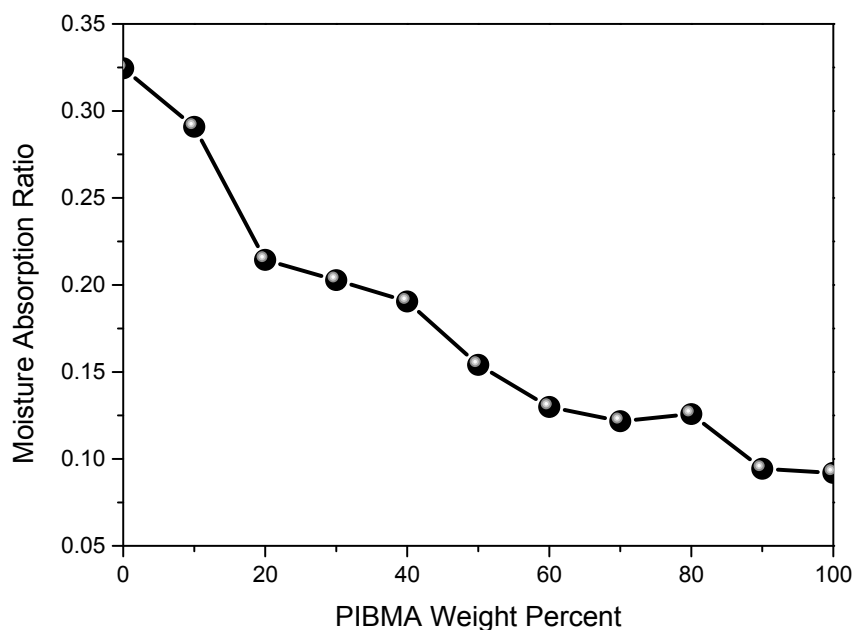
$$T_g = \frac{W_1 T_{g1} + kW_2 T_{g2}}{W_1 + kW_2} + qW_1 W_2 \quad (1)$$

where  $W_1$  and  $W_2$  are the weight fraction of each copolymer segment,  $T_{g1}$  and  $T_{g2}$  are the glass transition temperatures of each pure copolymer segment,  $k$  and  $q$  are fitting constants. Based on linear fitting,  $k = 1$  and  $q = 35$  were obtained in this study and the positive  $q$  value implies that these copolymers may possess the some interaction between PMMA and PIBMA, which is probably due to the dipole–dipole interaction between both carbonyl groups of PMMA and PIBMA polymer segments.



**Figure 1.** Glass transition temperature *versus* PIBMA weight fraction, predicted based on the Kwei Equation.

In addition, adding NDM prevented the gel effect and controlled the molecular weight. It was obvious that the molecular weights of these copolymers varied depending on the amount of mercaptan added. For example, molecular weights of  $1.4 \times 10^5$  to  $3.5 \times 10^5$  were obtained by adding 0.15–0.60 wt% of mercaptan. PMMA is highly moisture-absorptive because its carbonyl groups form hydrogen bonds with water; thus, its high moisture absorption restricts its optoelectronic field applications. Therefore, a bulky monomer that exhibits an excellent hydrophobic character is desirable. The water absorption analyses were performed according to the American Society for Testing and Materials (ASTM) D570 method. Figure 2 displays the plot of moisture absorption of the pure PMMA and a series of PIBMA-*co*-PMMA copolymers. After 24 h of the moisture absorption test, the moisture absorption content of the pure PMMA was approximately 0.32 wt% and the moisture absorption content was decreased with the increase of PIBMA contents in the PIBMA-*co*-PMMA copolymers that decreased to approximately 0.08 wt% for the pure PIBMA homopolymer. All moisture absorption data are also summarized in Table 1. This phenomenon proved that the PMMA copolymers fabricated by copolymerization with IBMA exhibited an improved glass transition temperature and lowered moisture absorption.



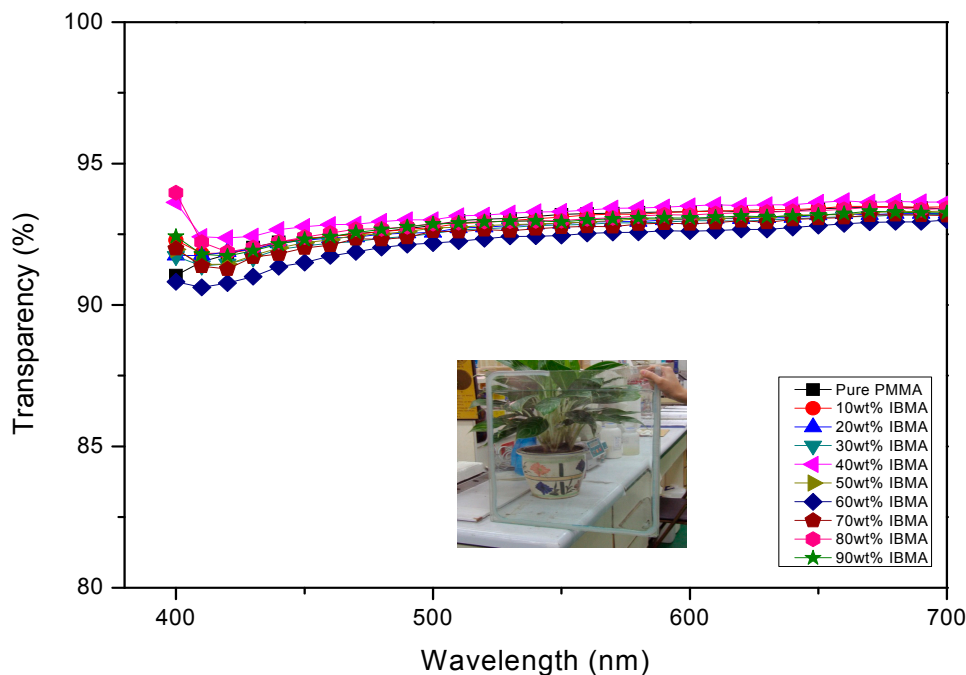
**Figure 2.** Moisture absorption ratio of PMMA-*co*-PIBMA copolymers.

**Table 1.** Characterization of PMMA-*co*-PIMBA copolymers.

| Copolymers <sup>a</sup> | MMA (wt%) | IBMA (wt%) | Moisture absorption (%) | Transmission (400–700 nm) | Yellow index | $M_n^b$ ( $\times 10^4$ ) | PDI <sup>b</sup> |
|-------------------------|-----------|------------|-------------------------|---------------------------|--------------|---------------------------|------------------|
| PMMA                    | 100       | 0          | 0.32                    | 92.6                      | 0.98         | 34.6                      | 1.20             |
| PMMA-PIBMA10            | 90        | 10         | 0.29                    | 92.9                      | 1.03         | 30.6                      | 1.25             |
| PMMA-PIBMA20            | 80        | 20         | 0.21                    | 92.4                      | 0.74         | 29.3                      | 1.26             |
| PMMA-PIBMA30            | 70        | 30         | 0.24                    | 91.8                      | 0.95         | 34.5                      | 1.23             |
| PMMA-PIBMA50            | 50        | 50         | 0.15                    | 92.4                      | 0.84         | 29.5                      | 1.22             |
| PMMA-PIBMA60            | 40        | 60         | 0.13                    | 92.2                      | 1.05         | 34.4                      | 1.24             |
| PMMA-PIBMA70            | 30        | 70         | 0.12                    | 92.1                      | 0.86         | 33.0                      | 1.28             |
| PMMA-PIBMA80            | 20        | 80         | 0.13                    | 93.1                      | 0.71         | 29.0                      | 1.25             |
| PMMA-PIBMA90            | 10        | 90         | 0.09                    | 92.1                      | 0.93         | 29.8                      | 1.24             |
| PIBMA                   | 0         | 100        | 0.08                    | 92.3                      | 0.92         | 28.1                      | 1.24             |

<sup>a</sup> Benzoyl peroxide as the initiator: add amount was 1.5 wt% based on the monomer weight; <sup>b</sup> GPC analysis with poly(methyl methacrylate) calibration.

The optical properties of the PIBMA-*co*-PMMA copolymers were analyzed using a spectrometer. The absorption of the bulk PMMA copolymer was determined using broadband optical transmission spectrometry in the range of 400–700 nm (Figure 3). The results obtained for the PIBMA-*co*-PMMA copolymers were distinct compared with those of the pure PMMA material, which exhibited a high transparency, particularly before 410 nm. In the range of 420–700 nm, PIBMA-*co*-PMMA copolymers exhibited optical profiles resembling those of pure PMMA polymers, indicating that copolymerizing IBMA with MMA enhanced the heat resistance and did not affect the color of the block material; this was attributed to the saturated ring of the IBMA.

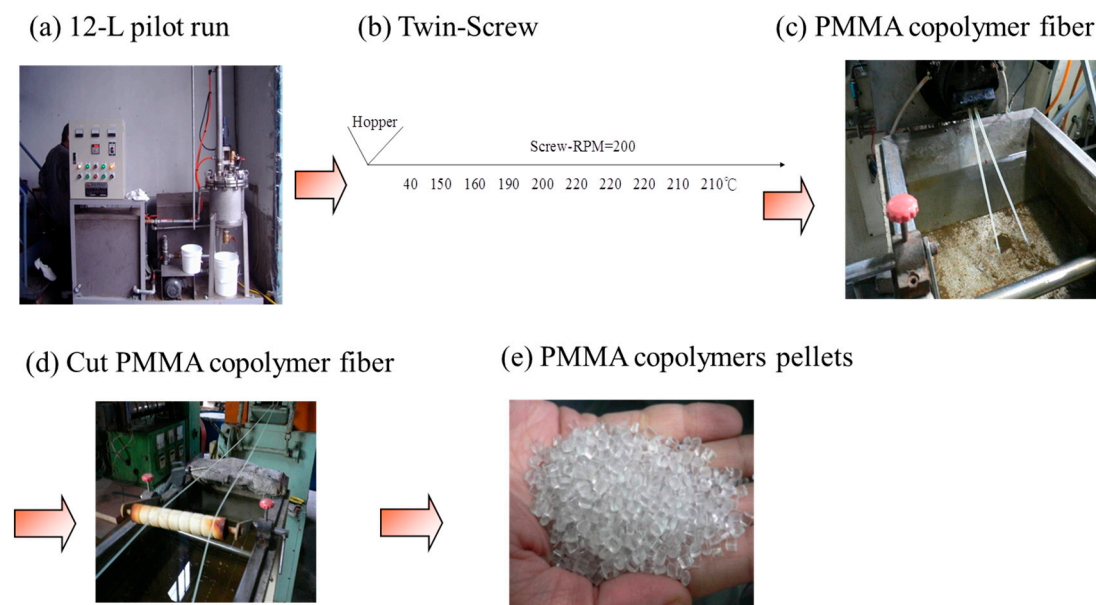


**Figure 3.** The optical properties of the PMMA-co-PIBMA copolymer. The inset figure is for real applications of PMMA-co-PIBMA copolymer.

Table 2 lists the compositions of the polymers after the reaction, namely the content of the main monomer MMA, bulky structure monomer IBMA, hydrogen-bond monomer methyl acrylamide, and chain transfer agent NDM. A two-stage copolymerization temperature program was adopted; the final product was detected by DSC and GPC. The data indicated that the copolymer exhibited excellent thermal properties and its molecular weight was suitable for use in extrusion processing. Therefore, the 12-L and 50-L pilot-scale production of raw materials was performed to determine the melting indices and moisture absorption ratios. The 12-L pilot runs of bulk polymerization were followed by extrusion granulation to obtain a transparent pellet that yielded a high glass transition temperature (Figure 4). Melt flow index measurements were performed in accordance with the ASTM D1238 standard. The melting index of the copolymer was 20.47 at 8.6 kg at 230 °C (PMMA-PMAA-PIBMA30).

**Table 2.** Two-stage copolymerization of MMA, MAA, and IBMA with 0.15 wt% NDM and 0.75 wt% I-BPO.

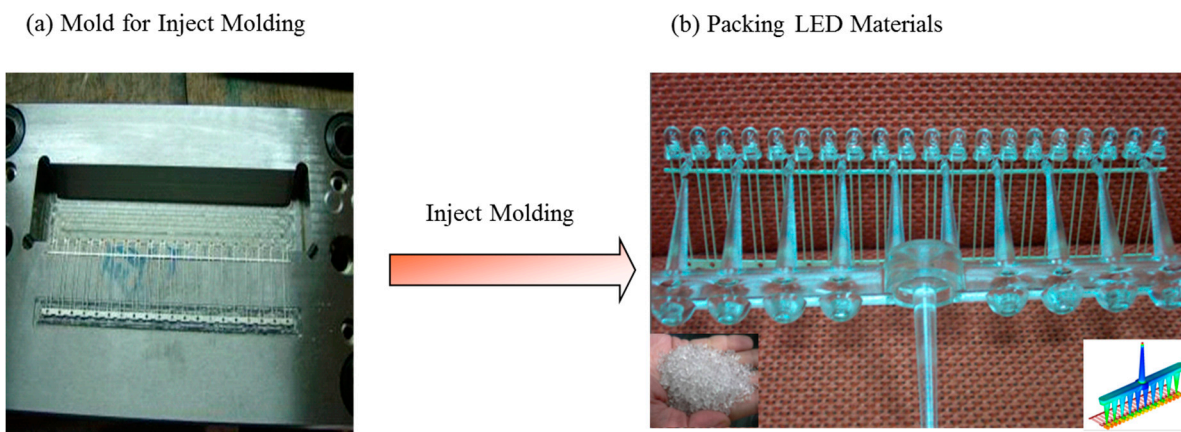
| Copolymers        | MMA (wt%) | MAA (wt%) | IBMA (wt%) | $M_w$ ( $\times 10^4$ ) | $M_n$ ( $\times 10^4$ ) | PDI  | $T_g$ (°C) |
|-------------------|-----------|-----------|------------|-------------------------|-------------------------|------|------------|
| PMMA-PMAA         | 92        | 8         | 0          | 17.8                    | 11.8                    | 1.50 | 107        |
| PMMA-PMAA-PIBMA30 | 62        | 8         | 30         | 18.4                    | 12.1                    | 1.52 | 128        |
| PMMA-PMAA-PIBMA35 | 57        | 8         | 35         | 16.7                    | 10.9                    | 1.53 | 138        |



**Figure 4.** The preparation of heat-resistant PMMA copolymer pellets.

The moisture absorption test was performed according to the ASTM D570 standard. Briefly, three samples of similar size were weighed using a balance that was accurate to three decimal places; the samples were dried at 50 °C for 24 h and soaked with water in an oven for 168 h to calculate the absorption content. After a week, the moisture absorption ratio of the pure PMMA was 0.66 wt%. The moisture absorption ratio of the PMMA-PMAA copolymer decreased to 0.46 wt%; and when IBMA was incorporated, the moisture content could be further reduced to 0.31 wt%. The transmittance was measured in a sample that was 50 mm × 10 mm × 50 mm (long × wide × thick), according to the Standard 1931 Commission Internationale Eclairage (CIE) colorimetric measurement, using the CIE standard illuminant C or A. The pure PMMA exhibited a 92% transmittance, whereas the PMMA-PMAA-PIBMA terpolymer exhibited a 90% light transmission, attaining optical specifications.

After increasing the content of IBMA to 30 wt%, the copolymer exhibited enhanced transparency and thermal properties and a suitable molecular weight for use in the extrusion processing. The molecular weight of this copolymer was less than 20 million, and the 12-L, 50-L, and 600-L pilot-scale production followed by extrusion granulation yielded transparent pellets that exhibited a high glass transition temperature, which is suitable for packing LED materials as shown in Figure 5. In summary, these PMMA-co-PMAA-co-PIBMA copolymer pellets synthesized using a controlled, rapid, and cost-effective method of bulky copolymerization, yielding an increased glass transition temperature, lowered moisture absorption, and enhanced optical properties.



**Figure 5.** The preparation of packing LED materials from heat-resistant PMMA copolymer pellets.

#### 4. Conclusions

A series of PMMA-*co*-PIBMA copolymers were prepared using bulk copolymerization by using chain transfer agents to generate the heat-resistance and transparency required for use in injection molding. The results indicated that the fabricated copolymers displayed both lowered moisture absorption levels and excellent optical properties. This novel thermoplastic material was fabricated by copolymerizing the IBMA monomer with MAA, yielding a transparency greater than 90%, excellent thermal resistance, and a moisture absorption ratio lower than 0.5 wt%. Thus, these copolymers are attractive for potential applications in packing LED materials.

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#### Author Contributions

Shu-Ling Yeh contributed to the synthesis of PMMA copolymers; Chao-Yuan Zhu and Shiao-Wei Kuo coordinated the study, interpreted the results and discussion, and contributed to the writing of the paper.

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