

Research Article

The Polymerization of MMA and ST to Prepare Material with Gradient Refractive Index in Electric Field

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Light scattering material with gradient refractive index was prepared under the electrical field by taking methyl methacrylate (MMA) monomer as the matrix with the addition of a little preheated styrene (ST) and peroxidation benzoin formyl (BPO). The material obtained under electrical field presented different transmittance and molecular weight at different parts of the cylindrical sample along the axis of the direction of electric field which led to the layering phenomenon and gradient refractive index. The disparity of molecular weight between different layers can be as much as 230 thousand. There were several peaks in the figure of GPC test of the sample under electric field. This proved that there were polymers with different molecular weights in the sample. Therefore, it can be concluded that electrical field has a significant effect on polymerization.

1. Introduction

There are at least two kinds of substance in light scattering material [1]. One is body material, the other is scattering material. The body material normally presents good light transmittance which guides light and forms the skeleton of light scattering material. In order to scatter light, the molecular polarity of the added scattering material should be different from that of the body material [2]. The content of the scattering material is much smaller than that of the body material. For example, polymethylmethacrylate/polystyrene (PMMA/PS) composite light scattering material is a kind of new light scattering material that has high transmittance and haze, which is widely used in polymer scattering elements and back light for liquid crystal display [3–7].

There are two methods to prepare light scattering material [8]. The first method is to copolymerize the monomers of two transparent polymers whose refractive indexes are different. This method often leads to phase separation due to poor compatibility. A more common operation is first to polymerize the scattering particle monomers and then swell

the scattering polymer in the body polymer's monomers, before finally polymerizing them together. The second method is to mechanically mix the transparent polymer body material with the scattering particle together. In comparison, the haze of the sample obtained from the first method could not be very large, while the transmittance of the sample obtained from second method is difficult to control.

Due to its excellent mechanical and optical properties, PMMA was always chosen to be a body material. PS was chosen to be scattering material because the refractive index of both PMMA/PS and MMA/ST had a gap. But when MMA and ST were mixed together to polymerize, copolymerization reaction [9] would occur, which may result in the decrease of haze. On the other hand, if we mechanically mixed PMMA and PS like the second method, the transmittance [10] could decrease to 20–30%. Furthermore, the mechanical properties of the sample would decrease due to the phase separation of PMMA/PS caused by mismatch of the polarity. For example, the impact strength could decrease to 1000 J/m², which was much lower than the pure PMMA sample. Therefore, the elimination of the phase interface was the key to prepare

the PMMA/PS light scattering material. In this work, we tried the first method which could prepare the light scattering material in polymerization method. In order to achieve the same scattering strength in all directions, the particle size and the refractive index of the light scattering material should be in gradient distribution.

The structure of the light scattering material was designed accordingly to meet the above requirements. It was shown in the studies that the size of scattering particle affected the optical property of the light scattering material [11–13]. The size of the scattering particle depended on the molecular weight of polymer. The higher the molecular weight, the bigger the particle size. So the size of scattering particle could be obtained by controlling the scattering monomer's polymerization degree. In the experiment, we first polymerized ST to get the prepolymer in different degrees of polymerization so that the molecular weight of the prepolymer ST was different and the polydispersity of the prepolymer was larger. Then we polymerized MMA and prepolymer ST to get the scattering particle PS and P(ST-MMA) in different molecular weights. So the degree of polymerization of the scattering particle PS and P(ST-MMA) was also in wide polydispersity, which may result in the various refractive index and polarizability. As the particles of different polarizabilities exerted different electric field forces in the gradient electric field, the particles in different molecular weights could be separated in gradient field to obtain the light scattering material with gradient refractive index.

This experiment took PS as scattering materials and PMMA as body materials [14] by using in situ copolymerization method [15]. The influence of the electrical field on eliminating the phase interface was studied during the preparation of the sample. We also did preliminary research on the property of the sample prepared in electrical field.

2. Equipment

American Waters company GPC apparatus: 515 HPLC Pump (precision 0.1% RSD), 717 Autosample, 2410 Refractive Index Detector, 996 Photodiode Array Detector, Millennium32, Styragel (HT3_HT5_HT6E). Situation: flow phase: furfuran (THF), velocity of flow: 1 mL/min, temperature: 30°C, standard sample: PS, molecular weight range: 500–3,000,000.

FESEM X-ray energy dispersive spectrum (EDX) XL30 S-EFG (Philips Company).

3. Experiment

3.1. Reagents and Purification

3.1.1. Reagents. The main reagents used in the experiment were MMA (analytical purity); BPO (analytical purity); ferrocene (98%); phosphoric acid (85%); anhydrous sodium carbonate (chemical purity); sodium borohydride (96%); anhydrous alcohol (analytical purity); petroleum ether (60°C–90°C), analytical purity; anhydrous ether (analytical purity).

3.1.2. Purification. Purification of MMA: firstly MMA was washed three times with 10% NaOH to remove inhibitor and

then washed another three times with deionized water. MMA was predried with anhydrous CaCl_2 and dried with CaH_2 . Then the MMA was distilled under reduced pressure with the existence of CaH_2 , and the middle distillation products were collected. Distilled monomer should first be vacuumed before being put in N_2 for protection and then kept in refrigerator for use at last.

Purification of ST: the same procedure and reagents as MMA are used.

Purification of BPO: firstly acetone was dehydrated with anhydrous K_2CO_3 before being distilled and collected between 55°C and 56°C. BPO was dissolved in the distilled acetone until saturation. Then the saturated filtrate solution was vacuumed till crystal appeared. The crystal was kept in refrigerator for 3 to 6 hours, and solvent was removed to dry the crystal. Finally crystal was protected with N_2 and kept in the refrigerator for use.

3.2. Sample Preparation. BPO (volume ratio is 0.5%) was put in the purified ST and polymerized in 60°C for 15 minutes in natural environment. The prepolymer ST was added to the mixture of MMA and BPO (volume ratio is 0.5%), and we kept the volume ratio of the prepolymer ST to be 0.2%.

The above polymerized system was kept about 20 to 25 minutes at 60°C. The prepolymer ST was under electric field (the electric field intensity is 5000 V/5 cm) [16]. The polymerization temperature was room temperature (approximately 27–31°C). The light scattering material with gradient refractive index was obtained until the polymerization system solidified [17].

4. Result and Discussion

During polymerization of MMA and prepolymer ST, the distribution of the BPO monomer (namely, the strength of BPO in different parts of the system) and prepolymer ST in the polymerization system were the primary factors that influenced the distribution of the final homopolymer and copolymer in the system. In PMMA body material, the refractive index of PS was different with the P(ST-MMA) copolymers and PMMA. When the light transmits in the material and encounters the PS scattering particle, the scattering happens. If the transmittance of the material was lower than 75%, the material could be produced as light scattering material [18].

4.1. Sample Figure and Colour. The sample figure of P(ST-MMA)/PS/PMMA prepared in natural environment (shown in Figure 1(a)) was compared with the sample prepared under electrical field (Figure 1(b)). The shape of the sample was cylinder with diameter of 15 mm and height of 40 mm. The vertical direction in Figure 1 was the cylindrical axial.

From Figure 1(b), it can be seen that the sample presented several layers along the cylindrical axial, which was consistent with the prediction in the introduction. Because every layer had different transmittance, the layering phenomenon occurred. The transmittance of the PMMA body material was very good; however in this material the layering phenomenon

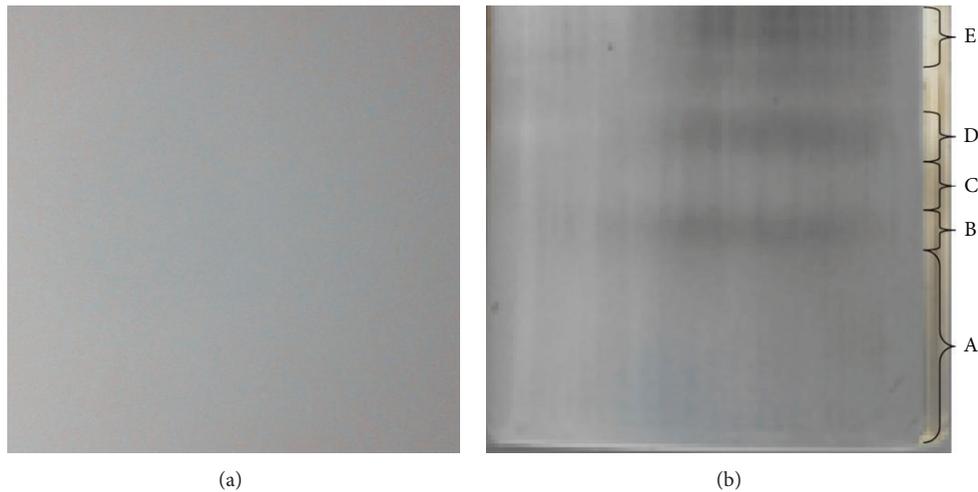


FIGURE 1: Layering phenomenon of the sample in natural environment and electrical field. (a) In natural environment. (b) In electrical field.

took place. The main reason was distribution of small amount of PS and P(ST-MMA) in the PMMA body material. PS and P(ST-MMA) were different from PMMA in refractive index and transmittance. As the content of the PS and P(ST-MMA) copolymer in different layers was different, the transmittance at different layers was different, which could result in the layering phenomenon. The ST and BPO monomers distribution varied in the polymerization system under the high strength electric field, which influenced the polymerizing process and the physical properties of the material, for example, transmittance.

4.2. Result of the GPC Test. From Figure 2, each layer of the sample contained three obvious peaks. One was big and the other two were small. It showed that there were polymers with different molecular weights in each layer, the big peak indicated polymer of high content and the small peaks indicated polymer of low content like PS. So we inferred that each layer had PS and P(ST-MMA) copolymer. Also the areas of the peak in each layer were different suggesting the different content of PS and P(ST-MMA) copolymer.

The transmittance of the layers depended on the content and compatibility of the polymers of different molecular weights in each layer. The results of the molecular weight test in different layers were shown in Table 1.

Based on Table 1, it can be concluded that the molecular weight and content of the PS and P(ST-MMA) in different layers were different. But the margin of the difference was just 0.1–1%. It indicated that the monomer ST and MMA were under different electric force in external electric field. When the polymerization was incomplete, the electric dipole moment of molecules in the solution was different which could cause the different displacement of the molecules under the gradient field. The electric dipole moment of the molecules could be arranged in the direction of the external electric field. As a result, the layering and the orientation phenomenon would occur in the sample. So the transmittance of the samples was different in the direction of cylinder axis.

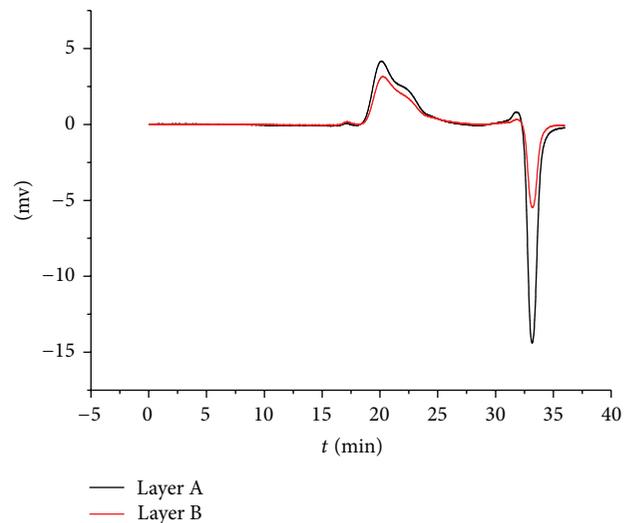


FIGURE 2: The GPC test result of layer A and layer B produced in electrical field.

The transmittance of layer A was smaller than other layers. It was because that the ST monomer had already prepolymerized for certain time, with PS already formed. However, due to the poor compatibility of the PS and PMMA and the huge refractive index disparity between two phases, the intertwined chain segment of the PS and PMMA led to huge interface area between two phases, which resulted in the small transmittance of the whole layers.

As layer B, from the test result of the GPC, the content of PS and P(ST-MMA) copolymer was more than that of layer A, but layer B's transmittance was higher than the layer A. The reason of this phenomenon was that the content of P(ST-MMA) copolymer was more than PS. The P(ST-MMA) copolymer was easily compatible with PMMA body material than PS, so the transmittance of layer B was better.

The rest of the layers also had different transmittance. The reason was the same with the mechanism studied above.

TABLE 1: PS and P(ST-MMA)'s molecular weight.

Layers of the light scattering (from bottom to up)	The bid peak's MP	The bid peak's Mn	The ratio of the small peak's area (%)	Haze (%)	Light transmittance (%)
Layer A	972237	787555	1.80	82.5	58.2
Layer B	1020879	678337	1.69	66.1	79.3
Layer C	1016391	665288	2.02	86.3	52.4
Layer D	1083097	888294	1.04	60.4	73.8
Layer E	1032240	677765	0.92	69.2	78.0

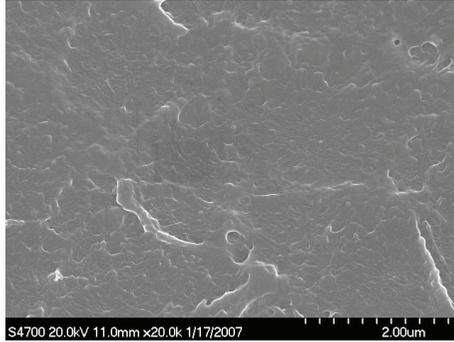


FIGURE 3: SEM microstructure of the pure PMMA sample.

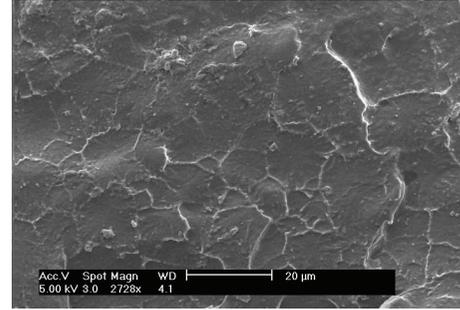


FIGURE 4: SEM microstructure of the section of layer A produced in electrical field.

The variety of the transmittance in different layers depended on the content of the two phases and the refractive index disparity between the two phases related to the two phases' compatibility. The compatibility of PS and PMMA body material was not good. But the compatibility of P(ST-MMA) copolymer and PMMA body material was much better. The copolymer forming factors were the content of the BPO and ST monomers. By controlling the electric field strength and the ST monomer polymerization time and distribution, the ST content could be changed in the system.

4.3. Information in the SEM Photograph. From Figure 3, no obvious structural characteristics could be seen. We could only see the unordered surface.

From Figure 4, the transmittance of layer A was little and the haze of this layer was high. The polymer chain section of the layer was small, while the configuration and appearance seem complex. The chain section distributed out-of-order and at long intervals there were some small particles. It showed that the PS content in layer A was higher. And the compatibility of PS and PMMA was not good. It resulted in the refractive index disparity between the two phases and the decrease of the transmittance.

Figure 5 showed microscopic configuration of layer B containing several small regions arranged disorderly. With improved degree of order in this layer, the chain section's integrity also increased. Clearly, less small particles are observed because P(ST-MMA) copolymer in layer B was more than that in other layers, and the compatibility between copolymer and PMMA was good. It leads to less disparity

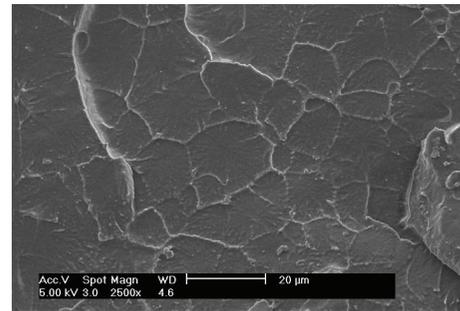


FIGURE 5: SEM microstructure of the section of layer B produced in electrical field.

of refractive index between two phases and higher transmittance.

Figure 6 was a 40000x photograph of small particles in Figure 4. It could be seen that the small particles were a node of the chain segment whose size was in range of micron meter and dispersed light intensively. It was the main matter which caused the light scattering.

The distribution of several scattering particles in PMMA body material could be seen in Figure 7. This distribution made scattering intensity uniform and let the material get good body scattering.

The SEM photograph showed the disparity of molecular structure of different layers which had different transmittances. The content of the PS or P(ST-MMA) copolymer dominated the layers' transmittance.

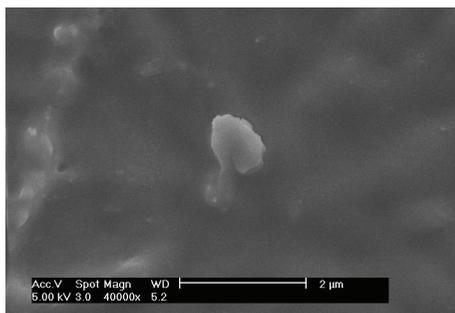


FIGURE 6: The configuration of the scattering substance.

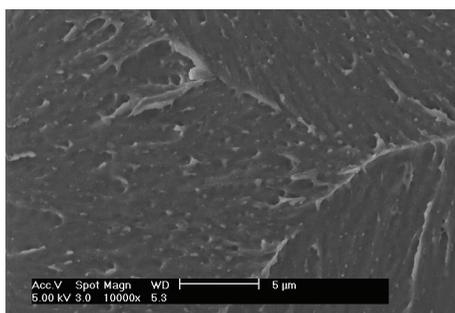


FIGURE 7: The distribution of several scattering material.

5. Conclusion

PMMA/PS light scattering material with gradient refractive index was prepared under electric field by in situ polymerization method. The material obtained under electrical field had different transmittance at different parts of the cylindrical sample along the direction of electric field which caused the layering phenomenon. The disparity of molecular weight between different layers could be as much as 230 thousand.

From the results of GPC and SEM, the difference between the samples obtained under electric field and natural environment was observed: the GPC test of the sample in natural environment had one peak; however the sample obtained under electric field had two peaks. The SEM results of the sample in natural environment indicated that chain section was out-of-order and the low-weight molecules were little. The SEM results of the sample obtained under electric field showed that chain section tended to be more regular with more low-weight molecules.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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