Living Free-Radical Emulsion Polymerization of Methyl Methacrylate (MMA) using a Surface Active Iniferter (Suriniferter): Polymerization Parameters and Molecular Structure of the Latex

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Abstract: A novel surfactant active RAFT agent as a suriniferter, composed of dithiobenzoyl main structure and benzoic hydrophobic/carboxylate hydrophilic moiety, was synthesized and applied to living radical emulsion polymerization of methyl methacrylate (MMA) initiated by UV irradiation in the absence of added surfactant and additional initiator at various temperatures. Stable spherical PMMA beads were successfully obtained using the suriniferter, maintaining the living radical polymerization characteristics, which shows a linear increase in molecular weight with respect to the conversion. The PDI varies from 1.21 to 1.43 and the final particle sizes vary from 407 to 304 nm with increase in polymerization temperature from 60 to 80°C. It is found that the polymerization is greatly retarded due to an increasing agitation speed. In addition, the increased agitation speed results in reduction of molecular weight and particle size without alternating the stability of the PMMA colloids. The triad tacticity of PMMA prepared with various concentration of suriniferter at several temperatures shows higher syndiotacticity in the range of 55.5–57.9% compared to commercial PMMA, inducing significantly high glass transition temperature. Thus, it is believed that the suriniferter used in living free radical emulsion polymerization modifies the stereoregularity of the PMMA.

Keywords: living radical polymerization, emulsion polymerization, RAFT, stereoregularity

Introduction

As the use of polymeric materials has been wide, the design of proper polymeric materials in molecular level has become of great importance. Owing to the advent of several revolutionized “living” radical polymerization methods, synthesizing well-defined polymers/copolymers having desired structures has come true in a convenient way, thereafter, the subject of molecular design of polymers by means of living radical polymerization has been a rapidly growing research area. These methods mainly include atom transfer radical polymerization (ATRP) [1,2], nitroxide-mediated polymerization (NMP) [3,4], and reversible addition-fragmentation chain transfer polymerization (RAFT) [5,6]. RAFT has several advantages over NMP or ATRP such as variety of applicable monomers at the same reaction temperature and method as in conventional radical polymerization without an additional catalyst removal process [7]. Therefore, the discovery of RAFT process is a breakthrough in the field of living radical polymerization.

In general in living radical polymerizations based on RAFT, various sulfide and disulfide iniferter (abbreviation of initiator-transfer agent-terminator) [8] are often used in conjunction with conventional initiator, to confer a living nature throughout the polymerization. Such iniferter are classified into photoiniferter bearing dithiocarbamyl group [9,10] and thermal iniferter carrying carbon-carbon [11,12] or azo [13,14] bonds according to dissociation locus.

Initial interests in living radical polymerization have been focused on the control of molecular architecture of polymers in bulk or organic media. However, this polymerization technique in aqueous media [15,16] is of great importance in industrial application because water
Scheme 1. Synthesis of 4-thiobenzoyl sulfanyl methyl benzoate.

as the reaction medium endows a number of advantages such as environmental-friendly process, easy removal of heat released during the reaction, and feasible handling of the final product. Since RAFT is readily applicable to emulsion or miniemulsion polymerization, intensive studies in water medium have been focused on this field [17-19]. Like conventional emulsion polymerization, ingredients for RAFT emulsion polymerization are water, water-insoluble monomers, water-soluble initiators, RAFT agents, and surfactants such as sodium dodecyl sulfate (SDS). The surfactant is responsible for the stability of latex by preventing coagulation between particles. However, when SDS is used with RAFT agents in emulsion polymerization, it significantly retarded polymerization rate and a deteriorated red layer of low molecular weight dormant species was observed in the beginning of polymerization, suggesting that interaction between SDS and RAFT agents [20] be occurring. In order to overcome the problems induced by surfactant, addition-fragmentation reactive surfactant, so called TRANSURF, has been designed. The basic structure of TRANSURF consists of three functional groups; methylmethacrylate dimer acting as a chain transfer agent, long aliphatic hydrocarbon chain responsible for hydrophobic moiety, and sulfate group attached to the hydrocarbon chain for hydrophilicity. TRANSURF is reported to behave as both chain transfer agent and surfactant in RAFT emulsion polymerization of PMMA [21].

In our present article, a novel surface-active RAFT agent, so called suriniferter consisting of dithiobenzoyl main structure, benzoic hydrophobic moiety, and carboxylate hydrophilic moiety, was synthesized and applied for preparing PMMA monodisperse beads using RAFT emulsion photopolymerization initiated by UV irradiation in the absence of added surfactant and additional initiator. Then, the polymerization characteristics, such as the conversion, molecular weight and its distribution, final particle size, and structural regularity of PMMA latex and its characteristics were studied depending on the suriniferter concentration and temperature.

Experimental Section

Materials
Reagent grade phenylmagnesium bromide, α-bromo-ρ-toluic acid, and carbon disulfide used in preparation of suriniferter were purchased from Aldrich Co. (USA). Anhydrous diethyl ether and methanol were purchased from J. T. Baker Co. (USA). Methylmethacrylate (MMA) was purchased from Junsei Chemicals, Japan. Carbon disulfide and diethyl ether were distilled for removing the existing water and impurities. MMA was distilled under reduced pressure to remove inhibitors and stored in a refrigerator prior to use. De-ionized (DDI) water was obtained by distillation of water twice and used as a reaction medium.

Synthesis of Suriniferter and Polymerization of PMMA
4-thiobenzoyl sulfanyl methyl sodium benzoate suriniferter was synthesized using the following three steps. First, 0.03 mol phenylmagnesium bromide and 0.045 mol carbon disulfide were reacted in dry diethyl ether at 10°C for 6 h. After removing unreacted reagents by distillation, 1:7:1 molar ratio of (thiobenzoyl)sulfanyl magnesium bromide and α-bromo-ρ-toluic acid were added in methanol. The second, the following reaction was carried out at 60°C for 24 h, then the unreacted reagent and methanol were removed by distillation. COOH end group of the product obtained from the previous reaction was replaced by -COONa by reacting with 1M of NaOH solution to introduce water-solubility of the product in order to utilize in emulsion polymerization. Detail for the synthesis procedure of the suriniferter is shown in Scheme 1.
Polymerization was carried out in a 500 mL four-necked reaction vessel with mechanical stirrer with agitation speed of 150 rpm. Polymerization temperature was carried out at 60, 70, and 80°C by controlling using water bath circulator and nitrogen atmosphere. 1kW UV lamp having 365 nm wavelength was employed to initiate the polymerization. The polymerization vessel was exposed to the UV irradiation throughout the polymerization. The concentration of methyl methacrylate (MMA) was 10 wt.% based on the reaction medium and the initiator concentration varied from 0.1 × 10³ to 1.0 × 10³ mol. The general procedure was as follows: DDI water and MMA were added in a reaction vessel and nitrogen was purged for 30 min. When the temperature of the reaction vessel reached a desired level, suriniferter dissolved in water was charged to the reaction vessel and the reaction was initiated by turning on the UV lamp. During the polymerization for 6 h, every 5 mL of sample was taken from the reaction vessel from time to time to characterize polymerization products. The conversion, the molecular weight and its distribution, and the intermediate particle morphology of the products were investigated. After completion of the polymerization, the resultant latex was frozen in a refrigerator and molten at room temperature. The precipitated phase was collected and dried in vacuo for 24 h. As a consequence, final white PMMA beads were obtained.

Characterizations

The chemical structure of the synthesized suriniferter and the obtained PMMA were confirmed by Varian 400-MHz ¹H-NMR using CDCl₃ as the solvent. Molecular weight and molecular weight distribution (polydispersity index: PDI) were characterized using Waters GPC (Gel Permeation Chromatography) equipped with 510 differential refractometer and Viscotex T50 differential viscometer. High-resolution columns packed with µ-styragel of 10⁴, 10⁵, and 10⁶ A pore sizes in series were employed. Universal calibration curve was obtained based on the measurements of elusion volume of ten polystyrene standard samples (Polymer Laboratories, UK) with given molecular weight ranging 750000~580 g/mole. PMMA powder dissolved in THF was injected at a flow rate of 1.0 mL/min. Scanning Electron Microscopy (SEM; Hitachi S-4300) was used to study the morphology of the synthesized PMMA particles. Differential Scanning Calorimetry (DSC; Perkin-Elmer DSC -7) was used to obtain the glass transition temperature of the PMMA. The monomer conversion to polymer was determined gravimetrically and the number-average particle diameter, dₙ, was obtained using Scion Image Analyzer Software by counting individual 100 particles from SEM microphotographs. The number of particles, N, was calculated from the following equation:

\[
N = \frac{6\pi W}{n d_D V}
\]  (1)

where \( x \), \( W \), \( D \), and \( V \) denotes the fractional conversion of monomer, the weight of monomers used, the density of polymer, and the volume of the reaction medium, respectively. The weight-average particle diameter, \( d_w \), was obtained from \( \sum n d_i / \sum n d_i^2 \), where \( n_i \) is the number of particles having diameter \( d_i \).

Results and Discussion

Scheme 1 shows the procedure of the synthesis of suriniferter that is used for the RAFT agent, consisting of 4-thiobenzoyl sulfanyl methyl sodium benzoate. The reaction solution turned out to be orange color when the first step of the reaction was completed, then the final yellow-colored powder was obtained by distillation. The chemical structure of 4-thiobenzoyl sulfanyl methyl sodium benzoate was confirmed using the proton NMR spectrum as shown in Figure 1. ¹H NMR : 4.7 (s, 2H, -CH₂-), 7.4-7.5 (m, 5H, ArH), 8.0 (m, 4H, -CH₂-ArH-).

The polymerization mechanism of this type suriniferter is suggested in Scheme 2, in which methyl benzoate group acts as an active growing species by generating a reversible addition-fragmentation mechanism. In the absence of conventional initiator such as potassium persulfate or ammonium persulfate, the generation of free radical is ascribed to the suriniferter by a homolytic cleavage of sulfur-carbon bond. Therefore, the term “iniferter” proposed by Otsu [8] would be appropriate for initiator in the absence of conventional initiator. In this case, radical is produced from the iniferter and the active
Scheme 2. RAFT Mechanism of MMA (M) in the Presence of Suriniferter.

radical is transferred to the iniferter itself, then a growing species is generated by a reversible addition-fragmentation mechanism. The active growing moiety further reacts with monomer and the radical is transferred to the dormant chain with dissociation of another radical that introduces termination. On the other hand, under the presence of initiator, the iniferter would rather act as a chain transfer agent, thus “RAFT agent” would be appropriate. Under UV irradiation on dithioester compounds, Hong and coworkers [22] suggested that the reversible termination mechanism would be applied for an explanation of living behavior. However, Quinne and coworkers [23] claimed that the reversible termination mechanism would not be adequate compared to the RAFT mechanism since it was not enough to differentiate between the two mechanisms regarding on the structure of the polymers obtained and account for the fate of radicals generated among the monomers.

Polymerization and Formation of Stable PMMA Colloid

In Figure 2, the number-average molecular weights of PMMA prepared by a constant 0.5×10⁴ mol of suriniferter are shown as a function of fractional conversion. It is noted that the polymerization recipe simply consists of water, monomer and the suriniferter since the suriniferter plays a role of initiator, chain transfer agent, terminator, and potential surfactant as well. Conversions of 0.85, 0.89, and 0.91 for 6 h of polymerization were obtained at 60, 70, and 80°C, respectively. This polymerization method using suriniferter and UV irradiation exhibits the characteristics of living radical polymerization by showing the linearity between the molecular weights and the conversion. In addition, the higher the polymerization temperature, the higher the molecular weight was obtained.
which is contrast to the behavior of macro-emulsion polymerization using thermal initiators [24]. In emulsion polymerization using conventional thermal initiators, molecular weight is subjected to decrease with initiator concentration since high concentration of free radicals were generated at high temperature by fast decomposition of thermal initiator, which results in facilitating bimolecular termination. The similar behavior was introduced in living free radical polymerization of poly-styrene using a RAFT agent by thermal initiation at a series of temperatures, thereby the number average molecular weight decreased with temperature [25] due to the same reason as described above. In controlled radical polymerization of styrene and acrylate by alkyl iodide degenerative transfer agent in the presence of AIBN, the effect of the molecular weight on polymerization temperatures between 50 and 90°C was insignificant [26].

Generally, the dependence of the number-average degree of polymerization on temperature shows an opposite result in radical thermal polymerization and photopolymerization, whereas the rate of polymerization behaves in the same way. As the temperature increases, number-average molecular weight decreases in thermal polymerization, and vice versa in photopolymerization [27].

Figure 3 represents the evolution of PDI values with respect to monomer conversion at various polymerization temperatures. The final PDI values were 1.23 (0.85 conversion), 1.29 (0.89 conversion), and 1.41 (0.91 conversion) at 60, 70, and 80°C, respectively. It is seen that the PDI values is not strongly influenced by the conversion, i.e. polymerization time, but tends to increase with polymerization temperature.

Figure 4 displays the SEM microphotographs of the PMMA beads prepared by living radical emulsion polymerization at 0.5 × 10⁻³ mol of suriniferter concentration at 60, 70, and 80°C. Again, it should be noted that additional surfactant or initiator such as potassium persulfate (KPS) was not involved in this figure. In the
presence of surfactant, polymer particles are formed in spherical micelle and continuously grow in size by monomer transport from its droplet that acts as a monomer reservoir. In surfactant-free emulsion polymerization, hydrophilic sulfate free radicals generated by the decomposition of persulfate react with hydrophobic monomer dissolved in the aqueous phase to form oligomeric free radicals, which can play a role of micelle formation [28]. The mechanism for the subsequent particle growth is the same as the case where a surfactant is employed. Surfactants are basically composed of hydrophobic and hydrophilic parts. The examples of hydrophobic moiety are long straight or branched alkyl groups, alkylbenzenes, and alkynaphthalenes. The examples of hydrophilic moiety include carboxyl (R<sub>COOM</sub>'), sulfonate (R<sub>SO<sub>3</sub>M</sub>''), or sulfate (R<sub>SO<sub>3</sub>2M</sub>'') for anionic surfactants, and quaternary ammonium halides (R<sub>4N</sub>Cl) for cationic surfactants [29]. For 4-diobenzyl sulfanyl methyl sodium benzoate used in this study, surface active group consists of hydrophobic benzyl and hydrophilic carboxyl moieties. By the homolytic cleavage of the carbon-sulfur bond in the suriniferer by UV irradiation, methyl benzoate radical as an active growing species initiates polymerization. The length of benzyl group in the surfactant moiety of the suriniferer seems short to play a role as surfactant in emulsion polymerization. In addition, the suriniferer itself cannot form micelles in the aqueous medium. However, as the length of oligomeric radical bearing the carboxyl end group becomes longer by further reaction of MMA through propagation, the degree of hydrophobicity is subjected to increase since the carbon-carbon bond on the oligomeric main chain is hydrophobic. This mechanism is similar to the surfactant-free emulsion polymerization as explained earlier where potassium persulfate, which is not a surfactant, can play a role of surfactant in the course of polymerization. The production of stable spherical PMMA beads prepared in this study is thus attributed to the suriniferer carrying the carboxyl group.

The particle size of PMMA beads prepared at 0.5 × 10<sup>-3</sup> mol of suriniferer concentrations at 60, 70 and 80°C is depicted in Figure 5. In all cases, stable spherical PMMA beads are successfully produced. These particles are formed from the early stage of the polymerization and grow subsequently. Since the lower the concentration of suriniferer, the lower the conversion was yielded at the same polymerization period, it is not appropriate to compare the dependence of the polymerization duration and temperatures on the particle sizes. In accordance with the temperature increase from 60 to 80°C, the particle size decreases from 407 nm to 304 nm, respectively, resulting a common observation in emulsion polymerization. In addition, the population of the particles increases with polymerization temperatures.

![Figure 5](image1.png)

**Figure 5.** The effect of temperature on the final size and the number of PMMA particles prepared with 0.5 × 10<sup>-3</sup> mol of suriniferer.

![Figure 6](image2.png)

**Figure 6.** The variation of the fractional conversion with respect to agitation speed in the polymerization of PMMA at 70°C.

**Effect of Agitation Speed on Polymerization**

In Figure 6, the monomer conversions for 1, 2, and 4 h are demonstrated as a function of agitation speed with 1.0 × 10<sup>-3</sup> mol suriniferer at 70°C. The polymerization seems to be greatly affected by the change of agitation speed. Above 280 rpm, the polymerization was significantly retarded thus the reaction medium remains transparent at 4 h as its original state. At agitation speed in the range of 120 ~ 250 rpm, turbidity was observed approximately 20 ~ 30 min after initiating polymerization.
Agitation in emulsion polymerization is known to possess its significance in several facets since it affects initial emulsification in the presence of surfactant, mixing of monomers for copolymerization, transport of monomer molecules to polymerization loci, temperature profile in the reactor and heat removal released from polymerization which is usually exothermic.

Several researchers have reported the retardation of the polymerization rate due to agitation speed in emulsion polymerization. Shunmukhan and workers [30] reported that fast agitation resulted in decreased overall polymerization rate and lowered molecular weight of the final polymer in emulsion polymerization of styrene. More precisely, Evans and workers [31] reported that the agitation speed exerted different effects in each interval of emulsion polymerization: In Interval I which is nucleation period, the rate of polymerization decreased with increasing agitation speed, in Interval II the rate of polymerization increased with increasing agitation speed, and in Interval III the rate of polymerization was not influenced by agitation speed. Regarding on the retardation of polymerization, Nomura and workers [32] found that emulsion polymerization is greatly influenced by the presence of impurities included in the nitrogen atmosphere. They concluded that oxygen in nitrogen gas would affect the retardation of the polymerization rate since agitation enhanced the adsorption of oxygen into reaction medium, which acted as a radical scavenger. They also claimed that an optimum range of agitation would exist, which would not affect the polymerization kinetics under an immaculate nitrogen atmosphere.

Figure 6 depicts that the retardation of the polymerization rate due to increased agitation speed is profound in this living radical emulsion polymerization of PMMA using the surfinerferter. It may be rationalized that the concentration of radical in this polymerization technique is much lower than in conventional radical polymerization. Therefore, the existence of oxygen significantly reduces the number of effective radicals participating in polymerization.

Figure 7 shows the number-average molecular weight, the molecular weight distribution, and the final conversion at 4 h polymerized with a 1.0 x 10⁻⁵ mol of surfinerferter at 70°C. The conversion linearly decreases from 0.91 to 0.54 with increasing agitation speed between 120 and 250 rpm due to the retardation of polymerization, resulting in corresponding decrease in number-average molecular weight. Whereas the molecular weight distribution slightly increases from 1.28 to 1.34 as agitation speed increases. A similar result has been reported in semicontinuous emulsion polymerization of styrene and butyl acrylate [33]. However, they reported that above 150 rpm, the conversion was not affected by agitation speed. This is contrary to our present system, which is mentioned earlier, the reaction was seriously retarded above 280 rpm and the reaction medium still remained in transparency in 4 h.

The dependence of the size of the PMMA beads prepared at various agitation speeds at 70°C is illustrated in Figure 8, showing that the particle size sensitively decreases with increasing agitation speed. In addition, the agitation speed applied in this experiment did not influence the stability of the PMMA colloids, thus all spherical discrete particles were observed without coagulation as seen in Figure 9.

**Stereoregularity and Thermal Properties of PMMA**

In Figure 10, the ¹H-NMR spectrum of the PMMA
prepared with $0.5 \times 10^{-3}$ mol of suriniferter at 70°C shows three distinct peaks occurring at the highest field, which represent methacrylate methyl groups with different tacticity [34]. The bands approximately at 0.82, 1.02, and 1.18 ppm are confirmed to attribute to syndiotactic (rr), atactic (mr), and isotactic (mm) methyl groups, respectively [34]. The tacticity of the PMMA was calculated by integrating the ratios of the rr, mr, and mm and the ratio of the triad tacticity for syndiotactic, atactic, and isotactic was 57.9, 35.9, and 6.1, respectively. To investigate the variation of the tacticity, polymerization temperature was changed from 60 to 80°C at a constant suriniferter concentration $0.5 \times 10^{-3}$ mol and the suriniferter concentration varied from $0.1 \times 10^{-3}$ to $1.0 \times 10^{-3}$ mol at a fixed polymerization temperature of 70°C. In all cases, the significant dependence of tacticity on polymerization conditions was not found. The triad tacticity was in the range of 55.5 - 57.9 for syndiotactic, 35.9 - 37.3 for atactic, and 6.1 - 8.3 for isotactic proportion. This result shows relatively high ratio of syndiotacticity compared to commercial molecular structure of the PMMA. As a result it is expected to affect the thermal properties. The triad tacticity of PMMA prepared at various polymerization conditions were calculated and summarized in Table 1.

In Figure 11, the DSC thermograms of PMMA obtained with a various concentration of suriniferter at various polymerization temperatures are demonstrated. As shown in Table 1, the glass transition temperatures ($T_g$) of the
Table 1. Triad Tacticity and the Glass Transition Temperature of PMMA Prepared at Various Amounts of Suriniferter and Various Temperatures

<table>
<thead>
<tr>
<th>No.</th>
<th>Polymerization Temperature (°C)</th>
<th>Suriniferter Concentration (x10⁻³ mol)</th>
<th>rr</th>
<th>mr</th>
<th>mm</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>0.5</td>
<td>57.2</td>
<td>35.9</td>
<td>6.9</td>
<td>128.8</td>
</tr>
<tr>
<td>2</td>
<td>70</td>
<td>0.1</td>
<td>55.7</td>
<td>36.0</td>
<td>8.3</td>
<td>127.9</td>
</tr>
<tr>
<td>3</td>
<td>70</td>
<td>0.5</td>
<td>57.9</td>
<td>35.9</td>
<td>6.1</td>
<td>129.1</td>
</tr>
<tr>
<td>4</td>
<td>70</td>
<td>1.0</td>
<td>56.8</td>
<td>36.4</td>
<td>6.8</td>
<td>129.3</td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>0.5</td>
<td>55.5</td>
<td>37.3</td>
<td>7.2</td>
<td>127.7</td>
</tr>
</tbody>
</table>

Figure 11. DSC thermograms of the PMMA beads prepared by various amounts of suriniferter and various temperatures.

synthesized PMMA lie in the range of 127.7 - 129.3°C. These values are much higher than that of the commercial PMMA (Tg = 105°C) [35] having 43% of syndiotacticity. The higher ratio of syndiotacticity results in relatively regular molecular structure, thereby leads to an increase in the glass transition temperature. In general, it is known that the glass transition temperature of PMMA greatly depends on the tacticity of the polymer, which is proportional to the content of syndiotacticity and inversely proportional to isotacticity. The glass transition temperature of PMMA was reported to increase from 41.5°C to 125.6°C for triad syndiotacticity/atacticity/isotacticity of 0/95/5 and 64/36/9, respectively [36]. Thus, we believe that the use of suriniferter using living free radical emulsion photopolymerization can induce different tacticity of PMMA.

Conclusions

A novel surface active RAFT agent as a suriniferter, composed of 4-thiobenzoyl sulfanylmethyl sodium benzoate was successfully synthesized and applied to RAFT emulsion photopolymerization of poly(methyl methacrylate) initiated by UV irradiation. No addition of further surfactant or initiator was applied. The polymerization characteristics, such as the conversion, molecular weight and its distribution, final particle size and its distribution, and molecular regularity depending on the suriniferter concentration and the temperature variation were studied. A linear increase in molecular weight with respect to the conversion is observed, indicating that emulsion photopolymerization using the suriniferter exhibits the characteristics of living radical polymerization. The PDI varies from 1.21 to 1.43 and the final particle sizes vary from 407 to 304 nm with increase in polymerization temperature from 60 to 80°C.

It is found that the polymerization is greatly affected by the change of agitation speed since increased agitation enhances the absorption of oxygen into reaction medium, which acts as a radical scavenger. The retardation of the rate of polymerization due to increasing agitation speed is profound in this living radical emulsion polymerization of PMMA using the suriniferter since the concentration of radical in living radical polymerization is much lower than in conventional radical polymerization. Above 280 rpm, polymerization is significantly retarded thus the reaction medium remains transparent at 4 h as its original state.

The conversion shows a linear decrease from 0.91 to 0.54 with increasing agitation speed from 120 to 250 rpm due to the retardation of polymerization, resulting in corresponding decrease in number-average molecular weight. While, molecular weight distribution slightly increases from 1.28 to 1.34 as agitation speed increases. In addition, agitation speed applied in this experiment does not influence the stability of the PMMA colloids so discrete PMMA particles without coagulation is successfully obtained.

The triad tacticity of PMMA prepared with various concentration of suriniferter at several temperatures is in the range of 55.5 - 57.9 for syndiotactic, 35.9 - 37.3 for atactic, and 6.1 - 8.3 for isotactic proportion. And the significant dependence of tacticity on polymerization conditions is not found. The glass transition temperatures (Tg) of the synthesized PMMA lie in the range of 127.7 -
129.3°C, which are much higher than that of the commercial PMMA (T_g = 105°C) having 43% of syndiotacticity. The higher ratio of syndiotacticity results in a relatively regular structure, thereby leads to an increase in the glass transition temperature. Thus, it is believed that the suriniferter used in living free radical emulsion polymerization modifies the tacticity of the PMMA.

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