

Shape memory behavior of poly(methyl methacrylate)-graft-poly(ethylene glycol) copolymers

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ABSTRACT

This paper describes a shape memory behavior of graft copolymers poly(methyl methacrylate)-graft-poly(ethylene glycol) (PMMA-g-PEG). In shape memory test, the sample was deformed from its original shape to a temporary shape above glass transition temperature (T_g), cooled below T_g to fix the temporary shape, and subsequently heated above T_g for spontaneous recovery to the original shape. By grafting PEG onto PMMA backbone, shape memory ability was drastically enhanced than PMMA homopolymer. The shape recovery ratio was decreased with the increase in the shape deformation temperature. With considering a good miscibility of backbone and side chain in PMMA-g-PEG, this shape memory ability may be related to a physically cross-linked network structure by chain entanglement of the comb-like graft copolymer. Stress relaxation measurements were investigated in order to confirm the effect of the graft chains on the shape memory behavior.

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1. Introduction

In recent years, shape memory polymers have drawn intensive attention because of their potential application as functional materials [1–4]. Shape memory polymers remember its original shape, and can recover from a deformed state when exposed to a stimulus such as heat. In most shape memory polymers, the original permanent shape is given by chemical cross-links. Mechanism of shape memory ability is schematically represented in Fig. 1. Deformation of the material can be achieved when a segmental Brownian motion of polymer chains is possible in liquid state, and this temporary deformed shape can be fixed when the segmental motion is frozen, i.e., solidification by glass transition or crystallization of the constituent polymers by lowering temperature. When the material is heated again above its glass transition temperature (T_g) or melting temperature (T_m), the segmental motion becomes possible again, and the material recovers to the original shape by an entropic force of the cross-linked polymer network. In these shape memory polymers, the cross-linking point is called as a fixing phase, and the component undergoes reversibly transition between liquid and solid state is called as a reversible phase. Recently, block and/or segmented copolymers consisting of hard and soft segments and forming microphase-separated morphology have been used as the shape

memory polymers. In these polymers, the segregated hard segments by physical interaction can act as the fixing phase, and the soft segments can be reversibly changed between vitrified glass state and rubbery liquid state [1–4].

It is well known that long branched or grafted side chains attached to main chain strongly influence a rheological behavior of polymer melt [5–16]. Mechanical properties of liquid-like polymers are dominated by an entanglement of polymer chains, because the entanglement points act as topological cross-linking points, which is an origin of the rubber elasticity of polymer melt. According to the tube model [5], reptation motion of the polymer backbone chain along the surrounding tube in branched polymers takes longer time than that in linear chain, as the result, the longest relaxation time drastically increases with length of branches. Because of these characteristics, branched polymers are commonly used to control the rheological behavior of polymer melt in industrial field such as polymer processing. If the entanglement point has much longer life time than the relaxation time of the segmental motion at the shape deformation temperature, it may be regarded as a physical cross-linking point during the deformation process. In this sense, branched or graft polymers have possibility to behave as shape memory polymers.

In our previous study, we have investigated morphology and crystallization behavior of graft copolymers, in which crystalline poly(ethylene glycol) (PEG) side chains are attached to amorphous main chain, for example, poly(methyl methacrylate) (PMMA) [17,18]. Because PEG and PMMA are known as miscible polymer pair, these poly(methyl methacrylate)-graft-poly(ethylene glycol)s

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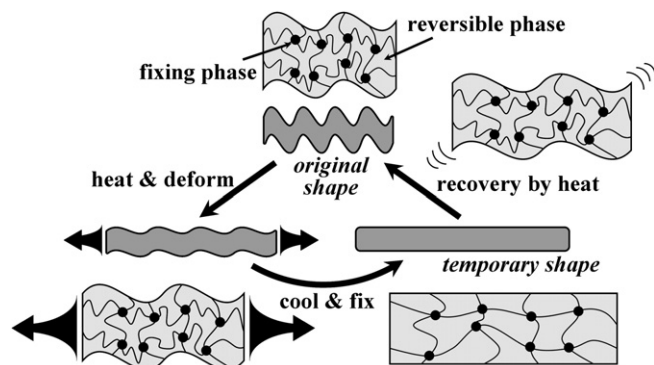


Fig. 1. Schematic representation of molecular mechanism for thermally induced shape memory behavior of network polymers.

(PMMA-*g*-PEG) were suggested to be in homogeneous phase without forming microphase separated domains above T_m of PEG [17]. So, the dynamics of PMMA-*g*-PEG chains may be described similarly with the branched polymers described above. PEG crystallization was suppressed because T_g of PMMA is higher than T_m of PEG, therefore, vitrification of PMMA-*g*-PEG with molecularly homogeneous phase occurred without side chain crystallization when PEG fraction was low. From these considerations, PMMA-*g*-PEG has a possibility to behave as a shape memory polymer with its entangled grafting points as the fixing phase and liquid–glass transition of the reversible phase of homogeneous PMMA/PEG.

In this study, we have investigated shape memory ability of graft copolymers PMMA-*g*-PEG with various graft densities of PEG side chain. The original film was deformed to a temporary shape at the temperature above T_g of PMMA-*g*-PEG, and subsequently cooled below T_g in order to fix the temporary shape. If the sample has the shape memory ability, the fixed temporary shape will recover to the original shape spontaneously by re-heating above T_g . Although the ability as the shape memory material was not enough, PMMA-*g*-PEG revealed more excellent shape recovery ability than the corresponding linear homopolymer. In the following sections, experimental results of shape memory tests for PMMA-*g*-PEG will be described, and discussed with considering the molecular architecture and melt rheology of the graft copolymers.

2. Experimental section

2.1. Sample preparation

Preparation of PMMA-*g*-PEG has been described previously [17]. PEG with a methoxy group at one end and a methacryloyl group at the other end (PEG-MA) was purchased from Aldrich as an aqueous solution. This PEG macromonomer was extracted into dichloromethane, and the organic layer was treated with aqueous NaOH and distilled water, dried, and precipitated in excess *n*-hexane. Number-averaged molecular weight (M_n) for the PEG block evaluated by ^1H NMR spectrum was 2000, and molecular weight distribution index (M_w/M_n , where M_w is weight-averaged molecular weight) for PEG-MA evaluated by size-exclusion chromatography was less than 1.1. Methyl methacrylate (MMA, Tokyo Kasei) was treated with aqueous NaOH and distilled water, dried, and distilled under vacuum. α,α' -Azobisisobutyronitrile (AIBN) was recrystallized from acetone.

Benzene solution of PEG-MA, MMA, and AIBN was bubbled by nitrogen gas, and free-radical random copolymerization was carried out at 60 °C. The polymerization was terminated when the solution viscosity began to increase. The polymerized solution was

poured into excess *n*-hexane. Unreacted PEG-MA and hardly-soluble microgel-like fractions were removed by repeated fractional precipitation by using 1,2-dichloroethane and *n*-hexane.

2.2. Characterization

M_n of PEG-MA and weight fraction of PEG in graft copolymer was estimated by ^1H NMR spectrum measured on a Bruker AVANCE200 using deuterated chloroform as solvent.

Differential scanning calorimetry (DSC) thermograms were recorded with a Perkin-Elmer Pyris1. Temperature was calibrated with indium and tin as standard. T_g of samples were evaluated from the second heating scan with the heating rate of 10 °C/min.

Evaluation of molecular weight was performed by size-exclusion chromatography (SEC) using a TOSO 8020. Tetrahydrofane (THF) was used as the eluent, and standard polystyrenes were used for molecular weight calibration.

2.3. Shape memory test

For shape-memory test, we have adopted two kinds of method, as described below.

2.3.1. Method I

1,2-Dichloroethane solution of PMMA-*g*-PEG was cast onto a PTFE plate and the solvent was removed at 100 °C for 2 days, and these films were stacked and pressed at $T_g + 70$ °C (110 ~ 170 °C). The obtained film was ~0.5 mm thickness, and annealed at $T_g + 50$ °C for 3 days before measurements. The flat strip specimen sized with 3 mm \times 32 mm was deformed to semicircle shape at a deformation temperature, T_{def} , which is higher than T_g , for 30 min. With maintaining at this temporary deformed shape, the film was cooled to -40 °C for 60 min in order for fixing the deformed shape. This semicircle film was moved into a thermostatic chamber regulated at a recovery temperature, T_{rec} , and its recovery behavior was observed. These processes are schematically illustrated in Fig. 2a. Shape recovery ratio, $R_{r,I}$, was defined by the following equation, in which the angles θ_1 – θ_4 are defined in Fig. 2b.

$$R_{r,I} = \left(1 - \frac{\theta_3 + \theta_4}{\theta_1 + \theta_2} \right) \times 100\%$$

If the sample recovered from the temporary deformed semicircle shape (i.e., $\theta_1 + \theta_2 = 90^\circ$) to the original flat shape completely,

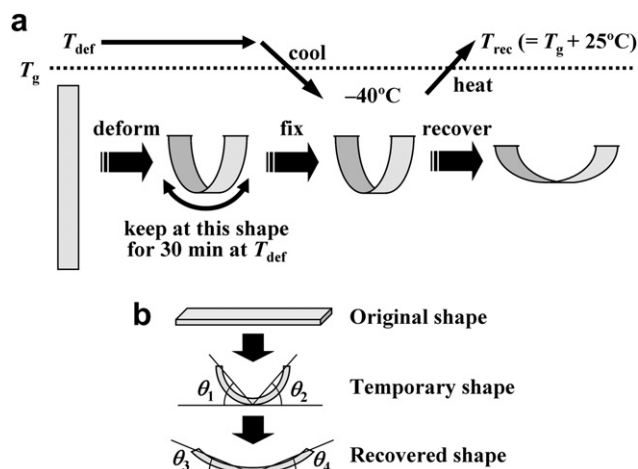


Fig. 2. (a) Schematics of shape memory test Method I. (b) Definition of angle θ_1 – θ_4 for evaluate shape recovery ratio $R_{r,I}$.

θ_3 and θ_4 will be zero by the elastic recovery at T_{rec} , so the value of $R_{\text{r,I}}$ will be 100%. In this case, the sample can be regarded to have the shape memory ability. On the other hand, if the sample was really deformed and fixed at the semicircle shape even after the heating at T_{rec} , $\theta_3 = \theta_1$ and $\theta_4 = \theta_2$, so $R_{\text{r,I}}$ will be 0%.

2.3.2. Method II

Because the samples used in Method I were rather thin, θ_3 and θ_4 were hard to be measured precisely when $R_{\text{r,I}}$ was close to 100% because the film was toppled over by recovering to almost flat shape. Therefore, an extensional deformation was performed in Method II. The solvent cast films were stacked and pressed at $T_g + 70^\circ\text{C}$ in order to obtain a flat film with 1 mm thickness. The sample sized with 1 mm \times 3 mm \times 30 mm was stretched to extensional strain of $\epsilon_1 = 60\%$ with a strain rate of 50 mm/min at the temperature $T_{\text{def}} > T_g$, and held for 120 min. With keeping this strain, the sample was cooled to room temperature ($\sim 25^\circ\text{C}$) for 60 min. After unloading, the length of the sample was measured and fixed strain ϵ_2 was evaluated. The unloaded sample was heated to T_{def} again, and the length recovered to the original one with elapsed time was measured to evaluate recovering strain ϵ_3 . Schematic illustration for this method is shown in Fig. 3. A shape fixity ratio ($R_{\text{f,II}}$) and a shape recovery ratio ($R_{\text{r,II}}$) were defined by the following equations.

$$R_{\text{f,II}} = \frac{\epsilon_2}{\epsilon_1} \times 100\%$$

$$R_{\text{r,II}} = \left(\frac{\epsilon_1 - \epsilon_3}{\epsilon_1} \right) \times 100\%$$

2.4. Stress relaxation

Stress relaxation curves were measured by using SEIKO DMS-6100. After stretching the film to tensile strain of 5%, residual stress at each elapsed time t , with keeping the initial strain, was measured, and relaxation modulus $E(t)$ was evaluated. The same measurement was performed at different temperature, and the obtained results at various temperatures were shifted as they were superposed with each other.

3. Results

3.1. Sample characteristics

The obtained PMMA-g-PEG was characterized by ^1H NMR and SEC in order to evaluate the mole fraction of PEG side chains and relative molecular weight. As listed in Table 1, the mole fractions of the PEG side chains are ranged from 0.6 mol% to 3.1 mol%. From the

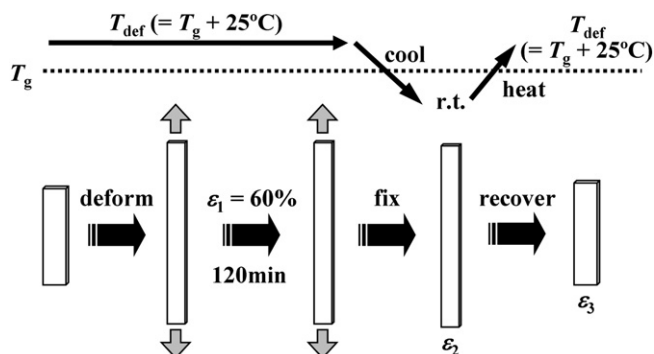


Fig. 3. Schematics of shape memory test Method II.

Table 1
Characteristics of PMMA-g-PEG.

| Sample code | M_w | M_w/M_n | Weight fraction of PEG / wt% | Mole fraction of side chain / mol% | $T_g / ^\circ\text{C}$ |
|----------------|---------|-----------|------------------------------|------------------------------------|------------------------|
| <i>l</i> -PMMA | 283,000 | 2.17 | 0 | 0 | 102 |
| PMMA-g-0.6 | 257,000 | 1.64 | 9 | 0.6 | 88 |
| PMMA-g-1.0 | 183,000 | 1.28 | 16 | 1.0 | 77 |
| PMMA-g-1.7 | 137,000 | 1.25 | 23 | 1.7 | 56 |
| PMMA-g-2.5 | 65,000 | 1.60 | 33 | 2.5 | 51 |
| PMMA-g-3.1 | 105,000 | 1.55 | 38 | 3.1 | 43 |

obtained SEC chart, we have confirmed that any unreacted PEG macromonomer and insoluble microgel-like particle were not contained in the final PMMA-g-PEG. The graft copolymers having higher PEG fraction revealed lower molecular weight, however, these values should be underestimated because of the low reliability in the molecular weight for branched polymers evaluated from SEC.

As mentioned in the previous report [17], PEG side chains in PMMA-g-PEG are hard to be crystallized because PMMA backbone and PEG side chain tend to be mixed homogeneously in the molten state. Therefore, in all the samples in Table 1, glass transition occurred before PEG crystallization during the cooling scan, and no crystallization peak was observed. In some samples, it was difficult to evaluate the T_g value precisely, in that case, Flory–Fox equation was used as support. The finally determined T_g values are also listed in Table 1.

3.2. Shape memory tests at various T_{def}

In the shape-memory test Method I, as shown in Fig. 2a, the sample film was deformed at T_{def} higher than T_g . After the deformation above T_g for 30 min, the sample was cooled to -40°C , enough lower than T_g , and the vitrification of the sample fixed the deformed shape. Even after the release of the force, the deformed shape was kept for at least 30 min. For homopolymer *l*-PMMA and graft copolymers PMMA-g-1.7 and -3.1, the shape memory test was conducted at various T_{def} , and the ratio of recovery ($R_{\text{r,I}}$) was plotted against the temperature difference from T_g , i.e., $T_{\text{def}} - T_g$, as shown in Fig. 4. If T_{def} is close to T_g , the polymer liquid exhibit rubbery elasticity because the entanglements of polymer chains act as physical cross-links, and it restricts a flow of the polymer chains

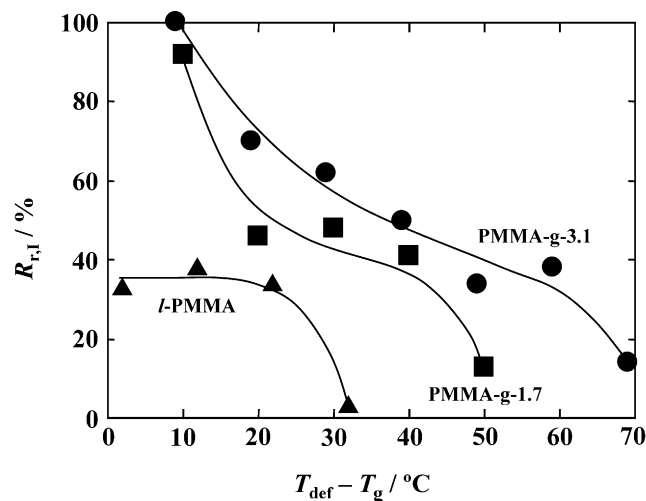


Fig. 4. Plots of $R_{\text{r,I}}$ against the temperature difference $T_{\text{def}} - T_g$ for (▲) *l*-PMMA, (■) PMMA-g-1.7, and (●) PMMA-g-3.1.

and maintain the original shape at this temperature. In *l*-PMMA, when T_{def} was equal to $T_g + 20^\circ\text{C}$, the original shape was recovered to about 40%, but the resulting sample could not be recovered to the original shape at $T_{\text{def}} = T_g + 30^\circ\text{C}$ because the applied stress was relaxed during the deformation for 30 min by the polymer chain flow. On the other hand, in the graft copolymers, $R_{r,I}$ values were about 50% even at $T_g + 30^\circ\text{C}$, suggesting a better shape memory ability in these samples. In PMMA-g-3.1, $R_{r,I}$ was still about 40% even at $T_{\text{def}} = T_g + 60^\circ\text{C}$. These results indicate that the grafted PEG chains effectively acted to remember the original shape even at the temperature above T_g .

In order to confirm the effect of the chain grafting, a blend sample of PMMA and PEG homopolymers was investigated. Polymer blend of *l*-PMMA/PEG (nominal $M_n = 2000$) with the weight fraction of 62/38 was prepared, and the results of shape memory test are shown in Fig. 5. Although the polymer composition for the blend sample was almost identical with that for PMMA-g-3.1, $R_{r,I}$ values of the blend at each T_{def} were much smaller than those for the graft copolymer. This result also suggests the side-chain grafting on the backbone is effective for the shape memory ability.

3.3. PEG content dependence on the shape memory ability

In order to evaluate the shape memory ability more precisely, the shape memory test Method II was conducted by applying the extensional deformation with $\epsilon_1 = 60\%$. According to the results in previous section, T_{def} was fixed to be $T_g + 25^\circ\text{C}$. In our preliminary experiment, we applied the above deformation for 30 min, which was identical with the Method I. The finally obtained shape recovery ratio $R_{r,II}$ for PMMA-g-0.6 and PMMA-g-3.1 was 97%, which means that the sample almost recovered to its original shape. However, the value of $R_{r,II}$ for *l*-PMMA conducted at the same condition was 81%. This high value even in the homopolymer suggests that the deformation time of 30 min was short in order to discuss the effect of the grafted chains on the shape memory ability. Therefore, in the Method II, we deformed the sample for 120 min at $T_{\text{def}} = T_g + 25^\circ\text{C}$ as mentioned in Experimental Section, in order to clarify the difference between the linear polymer and graft copolymer.

In all of the samples, values of the shape fixity ratio $R_{f,II}$ were almost 100%, i.e., at the room temperature below T_g , the deformed shape can be fixed completely by vitrification even after the release of the external stress. After that, the sample was re-heated to T_{def}

again, and the shape recovery behavior was measured with the elapsed recovery time. Thus obtained values of shape recovery ratio $R_{r,II}$ are plotted against the recovery time in Fig. 6. As shown in this figure, even in PMMA homopolymer, the shape recovery was observed but its shape memory ability was very low ($R_{r,II} < 25\%$). At the same condition, PMMA-g-PEG graft copolymers exhibited much distinct shape memory ability, i.e., by the introduction of only 0.6 mol% PEG side chains, $R_{r,II}$ reached at $\sim 70\%$ after 90 min.

Fig. 6 also indicates that the densely grafted sample exhibited smaller $R_{r,II}$ value than the sample with lower side chain content. In Fig. 7, $R_{r,II}$ values at 90 min are plotted against the mole fraction of the grafted side chains. This plot suggests that the highest shape recovery ratio was obtained at 1.0 mol%, and $R_{r,II}$ decreased gradually with the increase in PEG content. On the upper axis of Fig. 7, the averaged molecular weight of PMMA backbone between the most neighboring PEG graft chains, M_{inter} calculated from the PEG content, are indicated. The maximum of the plots is located around $M_{\text{inter}} = 10,000$, which is close to a reported value of molecular weight between an entanglement points, M_e , for PMMA (10,100) [19]. From these results, we can point out that the relaxation of the stress and polymer chain flow can occur more easily in the densely grafted PMMA-g-PEG than the copolymer with lower graft density when compared at the same temperature difference from T_g .

4. Discussion

The above experimental results indicate that the grafting of PEG side chains onto PMMA backbone drastically enhanced the shape memory ability. As described in Introduction, in common shape memory polymers, the original shape is stabilized by chemical or physical cross-links in order to prevent the polymer chain flow above T_g . The graft copolymers PMMA-g-PEG in this work is not covalently cross-linked, however, the junction point of backbone and side chain has a possibility to act as a physical cross-linking point. The entanglement of branched polymers is known to take much longer time to be disappeared by the reptation motion of polymer chains than that of linear polymers [5,11,12]. Molecular weight for the PEG side chain (2000) is slightly larger than M_e (1600) [19], therefore, the relaxation time for the terminal flow is expected to be increased. As the result, original shape with physically cross-linked polymer network by entangled graft copolymers can be memorized for a long time even at the temperature higher than T_g .

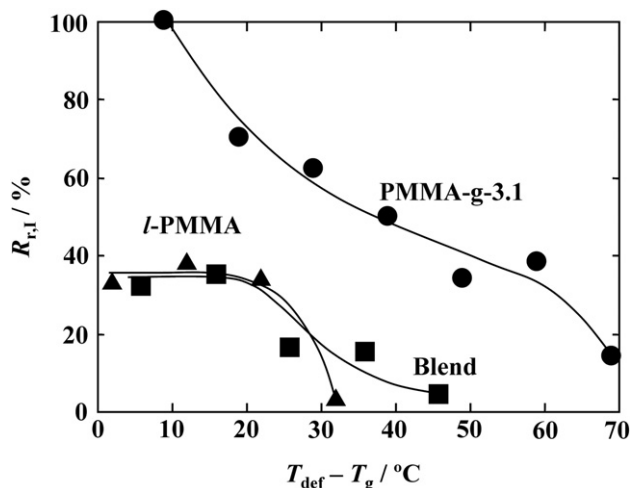


Fig. 5. Plots of $R_{r,I}$ against the temperature difference $T_{\text{def}} - T_g$ for (▲) *l*-PMMA, (■) blend of *l*-PMMA/PEG with the weight fraction of 62/38, and (●) PMMA-g-3.1.

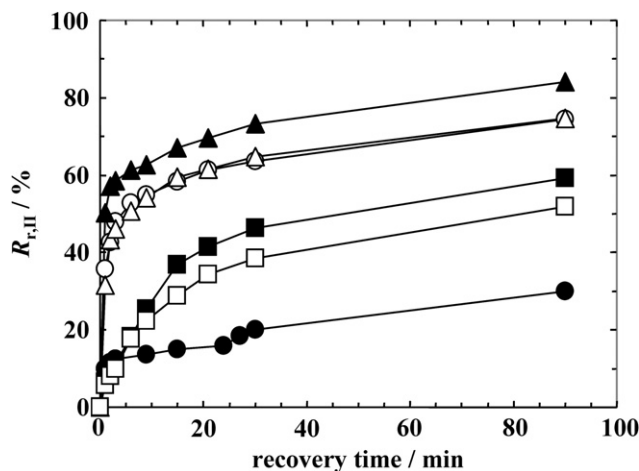


Fig. 6. Plots of $R_{r,II}$ against the time for shape recovery process. (●) *l*-PMMA, (○) PMMA-g-0.6, (▲) PMMA-g-1.0, (Δ) PMMA-g-1.7, (■) PMMA-g-2.5, and (□) PMMA-g-3.1.

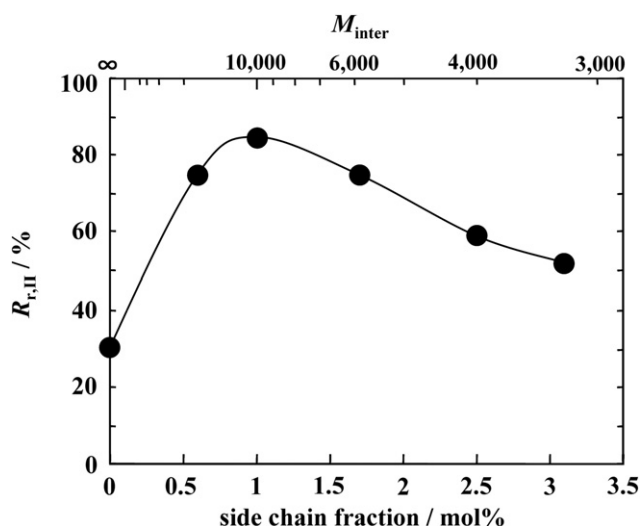


Fig. 7. Plots of $R_{r,II}$ at the elapsed time $t = 90$ min against side chain fraction (mol%) of each graft copolymers. At the upper horizontal axis, averaged molecular weight for backbone PMMA between the most neighboring PEG side chains, M_{inter} , is indicated.

In order to confirm the above consideration, we conducted stress relaxation measurements for PMMA-g-PEG graft copolymer, and compared with PMMA homopolymer. After an applied stress at $t = 0$, the relaxation stress was measured with an elapsed time at three different temperatures above T_g . Time-temperature superposition was applied by shifting the curve along time axis, and obtained master curves from rubbery plateau region to terminal flow region are shown in Fig. 8. For comparison of different copolymers having various T_g , $T_{def} = T_g + 25^\circ\text{C}$ was adopted as the reference temperature. As shown in Fig. 8, relaxation stress of *l*-PMMA exhibited sudden decrease before $t = 10^5$ s. On the other hand, in graft copolymers, such drastic decrease in $E(t)$ was not recognized within the measured time region ($\sim 10^6$ s). In the shape memory test Method II, the sample was deformed at T_{def} for 120 min = 7200 s. At this time, as indicated by hatched region in Fig. 8, the residual stress for *l*-PMMA was smaller than the other graft copolymers. Of course, the degree of deformation for the shape memory test was much larger than the stress relaxation measurements, this result indicates that the linear PMMA chain can

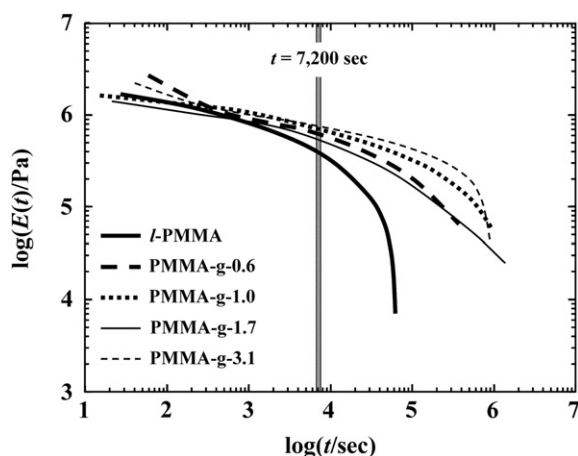


Fig. 8. Stress relaxation curves for *l*-PMMA and PMMA-g-PEG copolymers as indicated. The curves were obtained after time-temperature superposition conducted for the curves measured at different temperatures. Reference temperature for each polymer was fixed at $T_g + 25^\circ\text{C}$.

easily flow than the graft copolymer at $T_{def} = T_g + 25^\circ\text{C}$. In other words, the graft copolymer can remember the original shape for longer time and exhibit better shape memory ability than linear PMMA.

It should be noted that the deformation time of 120 min at T_{def} in the shape memory test Method II is fairly long, which results in the relatively low shape recovery ratio as shown in Fig. 6 ($R_{r,II} < 80\%$). As mentioned in Section 3.3, this experimental condition was determined in order to show the difference in the shape memory ability between linear PMMA and graft copolymers. Because the physical cross-links in the graft copolymer are caused by the entanglement of polymer chains, they would be disentangled at high temperature or after long elapsed time. Therefore, by adjusting T_{def} and deformation time appropriately, the graft copolymer can exhibit better shape memory ability than the present experimental condition. In our preliminary experiments, as commented in Section 3.3, the value of $R_{r,II} = 97\%$ was obtained for PMMA-g-0.6 and PMMA-g-3.1 when the deformation time was 30 min.

As shown in Fig. 7, the shape memory ability had the maximum around the graft density of 1 mol%, and decreased in more densely grafted PMMA-g-PEG. This result plausibly relates to the rheological behavior of branched polymers. Larson [13] pointed out that zero-shear viscosity (η_0) of branched polymer melt with same molecular weight is sensitive to the details of the branch distribution, i.e., η_0 was predicted to increase as an increase in degree of branching, α , and further increase in α induced a sudden decrease in η_0 . His prediction suggests a fast relaxation of polymer chain in densely branched polymers, which supports our PEG content dependence of shape memory ability in Fig. 7. Qualitatively, these trends might be explained by reduction of the degree of entanglements between backbone PMMA chains caused by the following reasons. (1) The attached PEG chains around PMMA sterically suppress the formation of entanglement between another PMMA backbone. (2) The side chain length is not so long ($\sim 1.25M_e$), so the influence on viscoelastic behavior by entanglements for the side chains might be small. As the result, the grafted PEG chain may act as diluent for PMMA backbone, which decrease the degree of entanglement. As mentioned above, the maximum in Fig. 7 located around $M_{inter} \approx M_e$. It seems reasonable that the shape memory ability and M_{inter} has a relationship, however, in order to confirm the reliability of the above relationship observed in this work, further experiments for other graft or branched polymer systems should be necessary.

There have been some references for shape memory polymers in which the chain entanglements are the origin of the physical cross-links [20–22]. As reported by Yang et al. [20,21], PMMA and other amorphous polymers such as polycarbonate exhibit impression recovery above T_g , and their results might be explained by the rubbery elastic recovery. As shown in Figs. 4 and 6, in our experiments, PMMA was found to exhibit weak shape recovery behavior after the large deformation. However, its temperature range was limited close to T_g , and introduction of a small amount of PEG graft chains was indicated to be effective to enlarge the relaxation time which substantially increased the shape recovery rate. In case of shape memory polynorbornene [22] having ultra high molecular weight ($>3,000,000$), chain entanglements were considered to act as physical cross-links, so the mechanism of the shape memory ability is very similar with our graft copolymers. However, to our knowledge, shape memory ability originating from the difficulty in disentanglement of graft or branched polymers has not been reported. Moreover, in contrast to the linear polynorbornene, our graft copolymers may possibly control the shape memory ability by tuning the molecular architecture and the consisting polymer block pair.

Liu et al. [23] have reported a shape memory polymer consisting of PMMA-PEG semi-interpenetrating polymer network (semi-IPN). In their system, MMA monomer and crosslinker (ethylene glycol dimethacrylate) was radically polymerized in the presence of linear PEG. The consisting polymers are identical, but in our system, PMMA and PEG chains are connected to form graft copolymers, and there are no chemical cross-links between the consisting polymers. The origin of the shape memory behavior in PMMA-g-PEG is physically-formed entanglement point acting as cross-linking point, which is different from semi-IPN PMMA-PEG.

Detailed structural and rheological studies for poly(*tert*-butyl acrylate-*g*-styrene) by de la Fuente et al. [24] showed that strongly segregated graft copolymers forming microphase-separated structure can be regarded as a physically cross-linked network. Shape memory effect of polyethylene/nylon 6 graft copolymers has been reported by Li et al. [25] In their system, the grafted nylon 6 blocks formed domains to act as physical cross-links, and crystallization of backbone polyethylene segment could fix the deformed shape. This mechanism in the network formation is principally the same with the block and/or segmented copolymers consisting of hard and soft segments.

5. Conclusions

Shape memory behavior of PMMA-*g*-PEG with various graft densities has been investigated. These polymers have no chemical cross-links, but demonstrated the shape memory ability; i.e. the original shape can be deformed at temperature above T_g , and this temporary shape can be fixed by vitrification below T_g . By heating above T_g again, the sample recovered from the temporary shape to the original shape spontaneously by the entropic elastic force of the deformed chain. In PMMA-*g*-1.7, the shape recovery ratio $R_{r,I}$ was much larger than PMMA homopolymer, indicating excellent shape memory ability. $R_{r,I}$ values decreased with increase in the deformation temperature T_{def} . These results may suggest that the shape memory ability is related to the physical cross-links by chain entanglement of comb-like graft copolymer.

Extensional deformation conducted at $T_{def} = T_g + 25^\circ\text{C}$ revealed that the $R_{r,II}$ value was highest when the graft density was 1.0 mol%, and decreased gradually with the increase in the graft density. This result was described by the decrease of entanglement between PMMA backbone because of the steric effect as well as the dilution effect by PEG side chains. Stress relaxation curve showed qualitative evidence of the better shape memory ability in the graft copolymers, i.e., higher relaxation modulus at the time corresponding to the deformation time and longer relaxation time for the terminal flow.

In graft copolymers in this work, the physical cross-link is considered to be formed by entanglement of polymer chains, so the obtained $R_{r,II}$ value was not so excellent than other reported shape memory polymers [1–4] because of the disentanglement during

the shape deformation for long time (120 min). Higher $R_{r,II}$ value was obtained in the experiment with shorter deformation time. This means that the permanent shape can be changed by long time deformation at high temperature, and the shape memory ability can be demonstrated by short time deformation at lower temperature. Therefore, by adjusting time and temperature appropriately, we can change the permanent shape freely, and its shape can be memorized to act as shape memory polymers. Additionally, the glass transition temperature of PMMA-*g*-PEG can be tuned by changing PEG composition because of the miscibility of PMMA and PEG, so the temperatures for processing, deformation, vitrification, and recovery can be adjusted for various applicable purposes. Shape memory behaviors for other branched polymers having different chemical and branched structures are in progress.

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