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Study of glass transition of Gd^{3+} doped poly(methyl methacrylate) by the internal friction method

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Gadolinium methacrylate containing poly(methyl methacrylate) ionomers (GMA-PMMA) and gadolinium octanoate containing poly(methyl methacrylate) (GOA-PMMA) have been synthesized. The investigation of their glass transitions was performed by the internal friction method. Although the internal friction at about 110°C for both samples showed a reduction when the Gd^{3+} content increased, differences have been found between the change tendencies, T_g and ΔE_a, of GMA-PMMA and GOA-PMMA as the concentration of Gd^{3+} increased. The behaviour of GMA-PMMA is similar to that of PMMA ionomers and the rates of change of T_g with ion concentration was found to be 15.6°C and 18.9°C per mol% of Gd^{3+} content at 0.7 and 0.1 Hz, respectively. A maximum T_g of GOA-PMMA appears at a 0.3 mol% concentration of Gd^{3+} and 0.7 Hz. Explanations are given in terms of structure differences, plastification of GOA and interactions between ions and PMMA chains, and a new model of multiplets is given for the GOA-PMMA sample based on this. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

The mobility of the main and side chains of macromolecules is one of the factors which determine the mechanical and other physical properties of solid polymers. The temperature dependence of molecular mobility is characterized by various transitions in which a certain mode of chain motion sets in. The most important transition in amorphous polymers is the glass transition temperature, T_g, at which the micro-Brownian motion of segments of the main chains become active. The glass transition has received much attention in polymer physics because it is accompanied by significant changes in the mechanical properties (the modulus of elasticity decreases by three or four orders of magnitude) and other physical properties of polymer samples; all of these are also important with respect to applications[1]. It is well known that ion-containing polymers perhaps provide an ideal system for the study of inter-molecular force since the interactions between ions can be quantified most precisely. For organic polymeric salts, one would see an initially rapid rise of the glass transition temperature with anion content, followed by a sigmoid shape with an accelerated rise of the glass transition and then another relatively lower rate of increase at still higher ion concentrations[2]. On the other hand, ion-containing polymers can be plasticized effectively with respect to backbone and ionic domain plasticizers. The former is the more conventional type in which the plastizing arises from the free volume effect (backbone plasticizers); the latter can act ideally by diminishing the interchain association of

the ionic groups on the polymer chain (ionic domain plasticizers)[3].

The internal friction method is a sensitive method and has been widely used to investigate the various low-frequency relaxation processes of solid materials in recent decades[4,5]. Under certain conditions, the internal friction method can be used to determine the glass transition, which is often called the α-transition, of amorphous solid materials. It has been found that α-transition can provide much information concerning the microstructure of polymers[6]. A study of the glass transition is also helpful in the investigation of the microstructures of ionomers or ion containing polymers as described above; however, no report has been found to perform the study using internal friction method.

Rare earth doped polymers have been paid more attention during recent years. One reason is that the polymer can be used in preparing functional polymer optical fibres, which have potential applications in all optical communication systems, as detailed in a recent study[7]. As rare earth ions are compatible with inorganic matrix, the rare earth ion doped silica glass could be made and the study of the photo-luminescence of this material started several decades ago[8]. However, due to poor solubility in an organic matrix, only in recent years has the study on rare earth ion doped polymer been carried out widely[9,10]. In order to change the situation mentioned above, two methods have often been adopted: the first involves the chelation of rare earths and then mixing with polymers[11]; in the second, the rare earth ions containing a monomer would be synthesized and then polymerized[12]. Another method has been developed in our laboratory. Rare earth octanoate, instead of a chelate, was synthesized according to a method reported before[13] and then mixed and polymerized with methyl methacrylate

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Table 1 Gd^{3+} content in ionomers based on poly(methyl methacrylate)[a]

	GMA1	GMA2	GMA3	GMA4	GMA5	
Gd^{3+} containing ionomers(mol%)[b]	0.3	0.5	0.8	1.0	1.3	
	GOA1	GOA2	GOA3	GOA4	GOA5	GOA6
Gd^{3+} containing PMMA (mol%)[b]	0.1	0.3	0.5	0.8	1.0	1.5

[a]AA content in polymer sample is about 11 mol%.
[b]Calculated in terms of the mole number of Gd^{3+} in each sample.

(MMA) monomers. Although polymers obtained in this way can be drawn into a fibre under high temperatures[7], detailed analysis on the relationship between the properties and structure of this polymer has not been carried out. In our work, Gd^{3+} octanoate (GOA) and Gd^{3+} methacrylate (GMA) were synthesized and then poly(methyl methacrylate) (PMMA) containing GOA and GMA was obtained according to a method reported before[7]. The dynamic mechanical properties of two polymers were measured by the internal friction method and different glass transition behaviours were found for GOA and GMA containing PMMA; the discussion is based on the micro-structures of these two polymers.

EXPERIMENTAL

Preparation of Gd^{3+} doped PMMA

Gd^{3+} doped polymers were prepared by a free radical polymerization which include two series of samples: one was doped with gadolinium methacrylate (GMA), the other with gadolinium octanoate (GOA). GMA and GOA were synthesized according to a method reported before[13]. The process of the polymerization is described below.

Different amounts of GMA (or GOA) were dissolved into acrylic acid (AA) and solutions with different Gd^{3+} contents were obtained. MMA was pre-polymerized in bulk with AIBN as initiator (0.2 wt%) for about 30 min and then mixed with salt solution (about 11 mol% of AA) under strong stirring. And then the polymerization was carried out in a tube at 50°C for 24 h and successively at 60, 70, 80, 90, 100, 110°C for 2 h to complete the reaction. The samples obtained in terms of the procedure were all hard and transparent and their Gd^{3+} contents are listed in *Table 1*.

Measurement

All samples were $1 \times 5 \times 15$ mm and polished to meet the need of the measurements of the low-frequency internal friction. The internal friction (IF) and relative shear modulus were measured by a multifunction internal friction pendulum (MFIFA-1, Institute of Solid Physics, Academia Sinica)[4], which could provide several different frequency measurements at one temperature running in the forced oscillation mode. The frequency was in the range 0.1–5 Hz and the heating rate was controlled at 1.5°C/min. The temperature measurement ranged from room temperature to about 150°C. All data can be shown by continuous curves rather than individual data points since many data points are collected, typically at the interval of 3°C. The X-ray diffraction spectra were determined on a Grigerflex D/MAX-γA rotating X-ray diffraction spectroscope with a copper target at an operating voltage of 40 kV and an electric current of 100 mA.

RESULTS AND DISCUSSION

White crystal particles of GOA were obtained by the
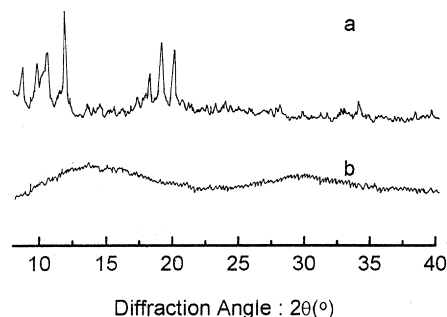
Figure 1 X-ray diffraction of: (a) gadolinium octanoate; and (b) GOA-PMMA. Gd^{3+} content, 2.4 mol%; thickness of sample plate, 1 mm

method reported before[13]. The wide-angle X-ray diffraction of GOA crystal is shown in *Figure 1(a)*. GOA can be dissolved in the solution of MMA and AA. According to the procedure described in Section 2, GOA containing polymer samples (GOA-PMMA) were made by the copolymerization of methyl methacrylate (MMA) and acrylic acid (AA), and GOA was blended into the samples forming a solid solution. *Figure 1(b)* shows that the diffraction of GOA disappeared in the X-ray diffraction of GOA-PMMA with 2.4 mol% of the Gd^{3+} content. This can be explained by the formation of the solid solution of GOA in PMMA at the given concentration range.

GMA containing PMMA (GMA-PMMA) was obtained by the copolymerization of three monomers: MMA, AA and gadolinium methacrylate (GMA). The copolymerization of MMA and AA has been studied and the reactivity ratios are 2.02 and 0.11, respectively, at 60°C[14]. A random copolymer structure with a longer chain of MMA units would be expected in terms of statistical analysis. Compared with MMA and AA, GMA is a monomer with a bulk substituent and would have a higher steric hindrance for another GMA to attack. This strong hindrance results from the large substituent on the alkene double bond, which decreases the possibility of its homopolymerization; GMA units then tend to be associated with other monomer units. In this way, GMA could expected to distributed in PMMA matrix homogeneously.

On the other hand, GMA contains three double bonds. Crosslinkings of intra- or intermacromolecular chains from GMA could be expected to exist in the samples. At the same time, because Gd^{3+} has a similar ion radius (0.94 Å) as that of Eu^{3+} (0.95 Å), it could have the multiple 7–9 coordinated types of sites and the lower site regularities of Eu^{3+}[15]. When introduced into copolymers, the flexible polymer chain would crowd around Gd^{3+} and the free carbonyl or ester groups would take part in coordination[16]. All these expectations appear to be in accordance with the following experimental findings.

The low-frequency internal friction probe (internal friction = IF, which has the same physical meaning as tan δ adopted in other mechanical spectroscopy) can be used
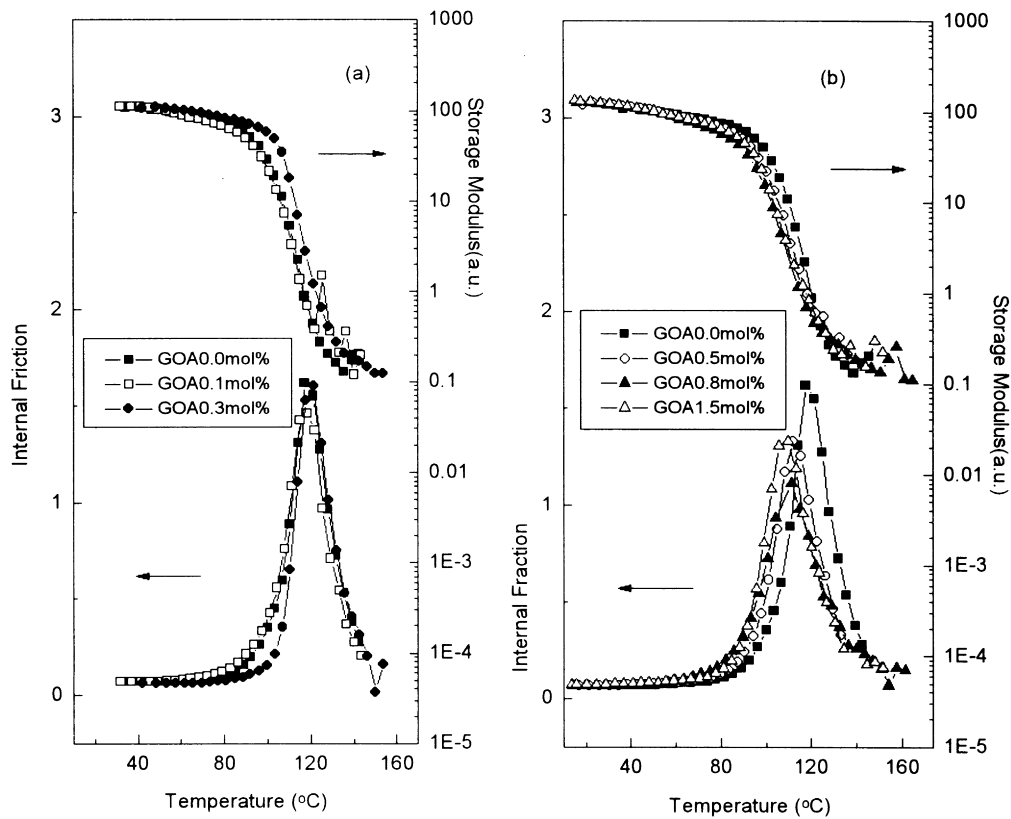
Figure 2 Internal friction and storage modulus curves *versus* temperature of GOA-PMMA at different concentrations of Gd^{3+} and 0.7 Hz
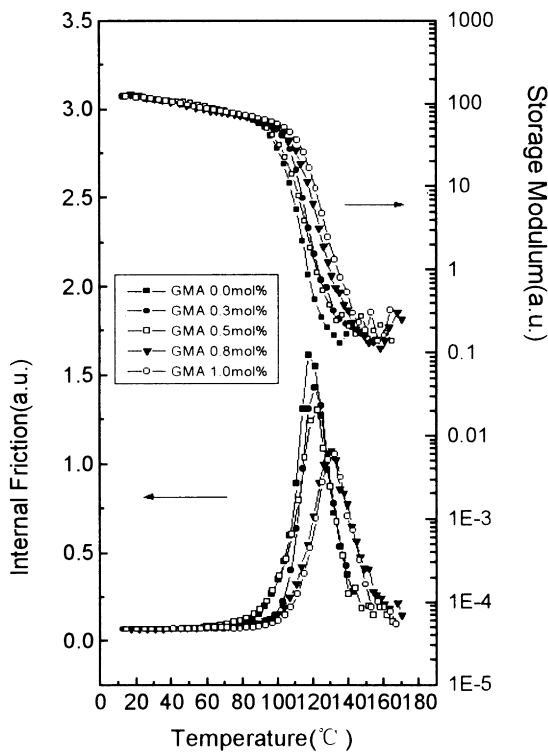

Figure 3 Internal friction and storage modulus curves *versus* temperature of GMA-PMMA at different concentration of Gd^{3+} and 0.7 Hz

to investigate the various relaxation processes of solid material samples and give several different frequency measurements with forced occillation mode within certain temperature measurement ranges. *Figure 2* shows, as a function of temperature and at the low frequency of 0.7 Hz, the results of IF for GOA-PMMA samples with various

Gd^{3+} concentrations. It can be seen that in the temperature range studied, there is only one IF peak for each sample, and with increasing Gd^{3+} content, the height of the peak decreases. When Gd^{3+} was doped into PMMA, the chain length or domains for the relaxation at given temperature would be further restricted by coordination actions of Gd^{3+} and become shorter or smaller, which would results in a decrease in IF. This phenomenon results from the stiffening of the matrix imparted by ionic domains has also been found in other systems[17]. Similar situations can be found in *Figure 3* from the values of GMA-PMMA's IF. GMA-PMMA is obtained by copolymerization of GMA, AA and MMA and each GMA can be considered as a crosslinking molecule. This crosslinked ionomer has a lower IF and a higher storage modulus with higher Gd^{3+} content (*Figure 3*). However, compared with each other in detail, there is a difference between the results shown in *Figures 2* and *3*: the peak of the IF shifts to a high temperature for GMA-PMMA samples, but to a high temperature first [*Figure 2(a)*] and then to a low temperature [*Figure 2(b)*] for GOA-PMMA samples.

It can easily be judged from the curve of the control sample in *Figures 2* and *3* that the relaxation process detected by the IF probe is the glass transition. The peak temperature for each sample at 0.7 Hz is adopted as the glass transition temperature (T_g) in this study. *Figure 4* shows the relationship between T_g and Gd^{3+} content of GMA-PMMA samples, from which an increase of Tg can be seen as the Gd^{3+} content increases. The lines shown have correlation coefficients of 0.9815 for 0.7 Hz and 0.9660 for 0.1 Hz and the rates of change of T_g with ion concentration are found to be 15.6°C and 18.9°C per mol% of Gd^{3+} content at 0.7 and 0.1 Hz, respectively. It has been found that in low ion content regions, the rate of change of T_g with ion concentration lies anywhere between 2°C and 10°C per
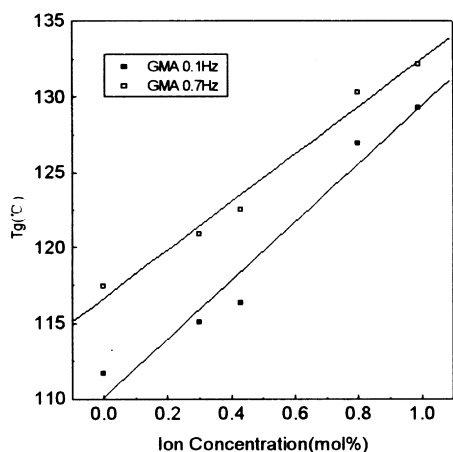
Figure 4 Relationships between the glass transition temperature (T_g) and ion concentration of GMA-PMMA samples at 0.7 Hz (□) and 0.1 Hz (■)
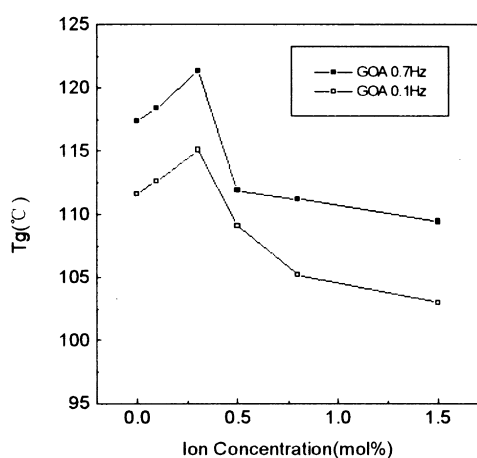

Figure 5 Relationships between the glass transition temperature (T_g) and ion concentration of GOA-PMMA samples at 0.1 Hz (□) and 0.7 Hz (■)

mol%[18]. The higher value for GMA-PMMA results from the use of ion concentration in *Figure 4* rather than charge concentrations. A study of the T_g of sulfonated polystyrene–metal ionomers has shown that the T_g values of the ionomers depends only on the sulfonation level despite wide variation in metal ion charge and size[19]. The rate of T_g changes is 5.2°C per mol% for GMA-PMMA samples at 0.7 Hz if charge concentration is used instead of ion concentration in *Figure 4*. This is nearly equal to 5.5°C per mol% of Na^{1+} containing PMMA ionomers[20]. The different changing tendency of T_g has been found in *Figure 5* for GOA-PMMA samples. When ion concentration is lower than 0.3 mol%, T_g increases with increasing ion concentration. This is identical with the general situation of ionomers. However, after 0.3 mol% concentration, T_g decreases to a level of about 105°C, which is nearly 10°C lower than T_g of the control sample, with increasing of ion concentration. It is more interesting that IFs of GOA-PMMA are also decrease with increasing of GOA content in the same way of GMA-PMMA.

Generally speaking, plasticization of an ion containing polymers includes two aspects: one is the more conventional type where the plasticizing effect arises from free volume effects and is usually called backbone plasticization; the other acts ideally by diminishing the interchain association of the ionic groups on the polymer chain and is called ionic domain plasticization. It has been found that ionic domain

plasticization cannot cause a reduction of T_g and tan δ of ionomers[21]. Although coordinations can also take place between Gd^{3+} and the free carbonyl or ester groups in the flexible polymer chains because Gd^{3+} could have multiple 7 to 9 coordinated types of sites[16], the backbone plasticization of GOA can be expected from the results in *Figures 2* and *5*. GOA is a long chain aliphatic ester which is not compatible with PMMA chains. This structural characteristic would result in small phases composed of GOA molecules being distributed in the PMMA matrix. According to the observation described above, the phase can be considered as multiples rather than a cluster because the concentration of GOA is low. An increase in the free volumes of polymers imparted by incompatibility between two phases causes a reduction in the T_g of GOA-PMMA. In practice, taking all points in *Figure 5* into consideration, it can be deduced that coordination and plasticization both exist in GOA-PMMA samples. The maximum T_g is reached by equilibrium between these two opposite effects. It is worth noting here that this micro-phase separation become macro-sensible when Gd^{3+} content is over 2.5 mol%, as found in our experiments. In a low concentration range, the distance between two Gd^{3+}s in GOA-PMMA is closer than that in GMA-PMMA, as confirmed by fluorimetry analysis[22], which shows that GOA could move freely as an additive in GOA-PMMA and cause a sensible plasticizing effect. On the other hand, a decrease in the IFs of GOA-PMMA when the GOA content increases shows that the coordination action is the same in two systems; that is say, the contribution of each Gd^{3+} for the coordination would be equal to each other. Based on this phenomenon, a new multiplet structure can be expected: ions are on the out-surface of the multiplet and long aliphatic chains of GOA compose the core of the multiplet because they are not compatible with the polar matrix of PMMA. A schematic diagram of the multiples model can be found in *Figure 6*.

The absolute values of IF in *Figures 2* and *3* are also identical with the result evaluated above. For GMA-PMMA, the rate of decrease in IF is larger than that for GOA-PMMA. This shows that coordinating actions are stronger in GMA-PMMA samples, which arises from a more
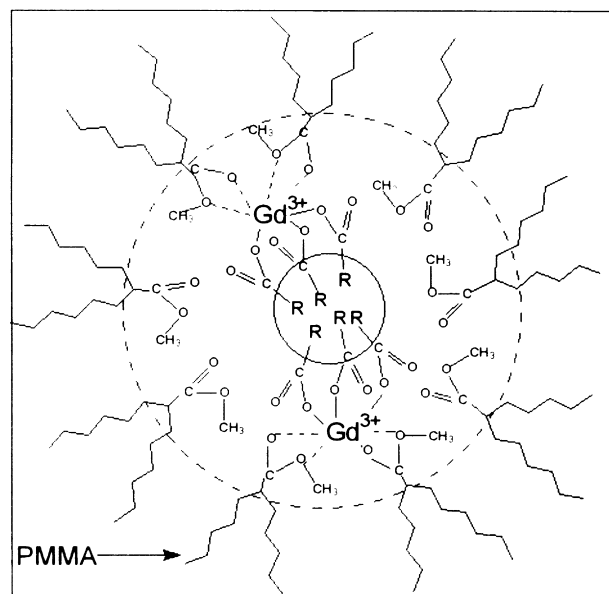
Figure 6 Schematic representation of the multiplet model of GOA-PMMA
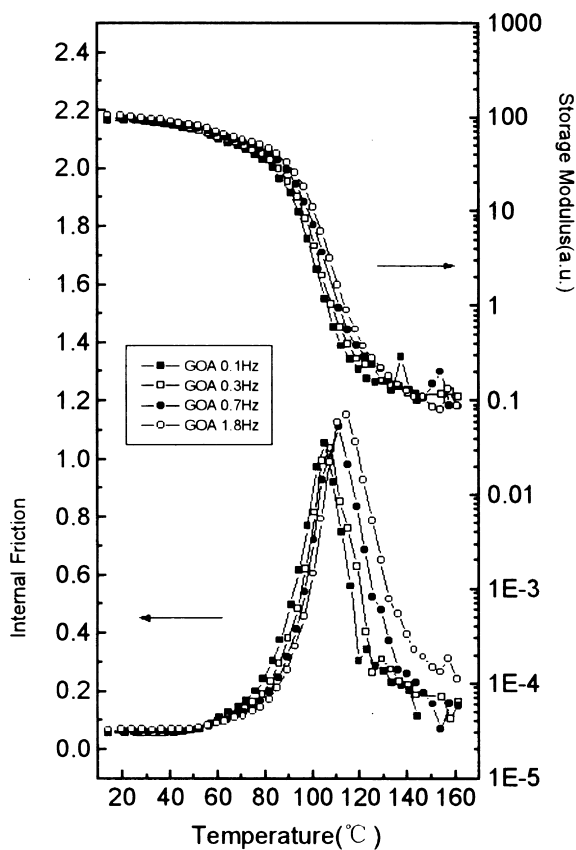
Figure 7 Internal friction and storage modulus curves versus temperature of GOA-PMMA at different frequencies and Gd^{3+} concentrations of 0.8 mol%
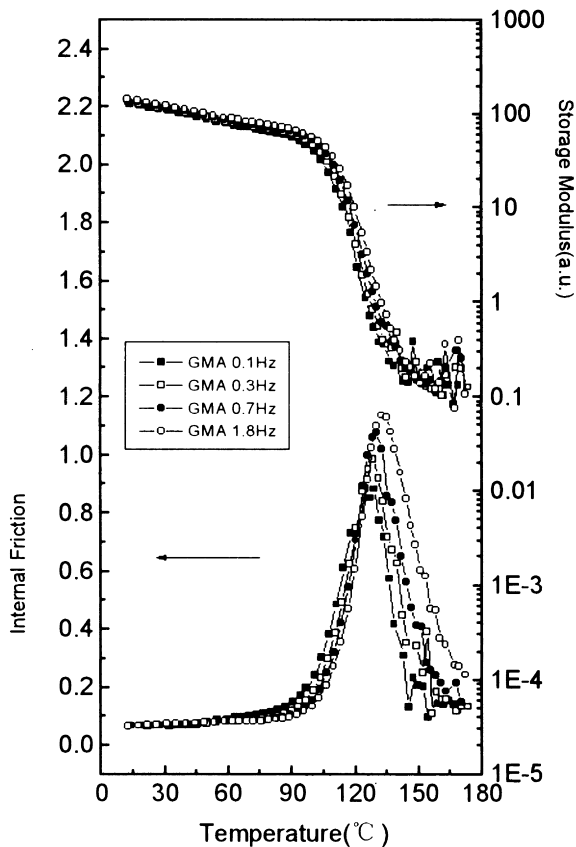

Figure 8 Internal friction and storage modulus curves versus temperature of GMA-PMMA at different frequencies and Gd^{3+} concentrations of 0.8 mol%

homogeneous distribution of Gd^{3+}. A single ion cross-linking point would be expected for this sample. However, two or more ions could be included in a multiplet. The coordinating actions are weaker for the sample containing the multiplet, although the action of one single ion for the coordinating is the same in GMA-PMMA and GOA-PMMA samples.

It is well known that the position of the peak in dynamic experiments is a function of the frequency of the experiment[18]. At a Gd^{3+} concentration of 0.8 mol%, *Figures 7* and *8* show the IF at different frequencies of GOA-PMMA and GMA-PMMA, respectively, from which it can be seen that IF all decrease with the decreasing frequencies used in the experiments for both systems. At the same time, the positions of the IF peaks show a sensible change in the same one direction: the position of the peak (T_g) moves to a lower temperature as the frequency decreases. Corresponding to the IF peaks, the slope of the modulus curves have a relevant change too. Based on the character of the above experimental results, it can be deduced that the relaxation is a typical glass transition process and a kinetic phenomenon, which may very well has underlying thermodynamic reasons. Thermal activation of the relaxation generally follows the well-known Arrhenius law, where the activation energy for the relaxation (ΔE_a) could be calculated from the slope in the plot of $\ln \omega$ *versus* $1/T_g$ which can be expressed as follows:

$$\ln \omega = \ln \omega_0 + \Delta E_a / RT_g$$

in which ω is the frequency and T_g is the glass temperature correspondmg to the maximum value of IF in the plot of IF *versus* temperature at any frequency[23]. *Figure 9* shows the Arrhenius plots of $\ln \omega$ *versus* $1/T_g$ for GOA-PMMA and GMA-PMMA, respectively. The activation energy of transitions from the slopes of Arrhenius plots are given in *Table 2*. In GMA-PMMA system, there is a sensible increase of ΔE_a when the concentration of GMA increases. This is because Gd^{3+} ions are distributed in the PMMA matrix more homogeneously, as mentioned in the discussion, based on the synthesizing process, and the extent of the ion crosslinking would increase the same as T_g as the concentration of Gd^{3+} increases. On the other hand, although Gd^{3+} in GOA-PMMA has the same coordination actions as Gd^{3+} in GMA-PMMA, GOA could move in
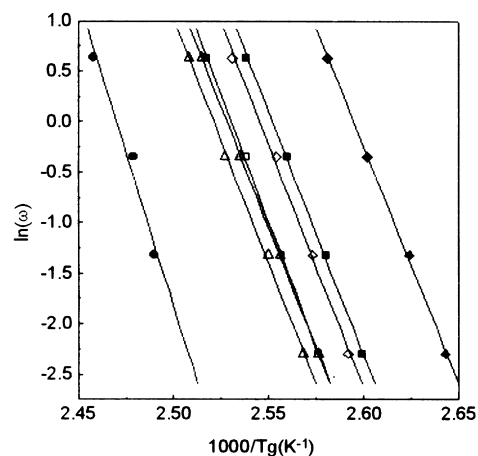
Figure 9 Plots of ln(frequency) *versus* $1/T_g$ for control sample (■); GMA-PMMA samples at Gd^{3+} concentrations of 0.3 mol% (□), 0.5 mol% (△), and 0.8 mol% (●); GOA-PMMA samples at Gd^{3+} concentrations of 0.1 mol% (◇), 0.3 mol% (▲), and 0.8 mol% (◆)

Table 2 Activation energy of glass transition for GOA-PMMA and GMA-PMMA

Concentration of Gd^{3+} (mol%)	ΔE_a (kJ/mol)	Correlation coefficient
0.0 mol%	400.9	0.999
GOA 0.1 mol%	401.5	0.999
GOA 0.3 mol%	398.5	0.999
GOA 0.8 mol%	390.6	0.999
GMA 0.3 mol%	414.9	0.999
GMA 0.5 mol%	399.6	0.999
GMA 0.8 mol%	501.7	0.999

PMMA and a multiplet composed of more than one GOA could be formed as given in the model described above, which has also been observed by fluorimetry measurements reported before[22]. This may cause a reduction in the T_g shown in *Figure 5* and also a slight reduction of ΔE_a within the given concentration range.

CONCLUSIONS

Gadolinium methacrylate containing poly(methyl methacrylate) ionomers (GMA-PMMA) and gadolinium octanoate containing poly(methyl methacrylate) (GOA-PMMA) have been synthesized. Analysis of X-ray diffraction on these sample has shown that diffraction peaks of the crystals have disappeared when they are doped into the PMMA matrix at the given concentration range. Statistic analysis on copolymerization can also expected that GMA is distributed in PMMA more homogeneously than GOA.

An investigation of the glass transitions of GOA-PMMA and GMA-PMMA was performed by the internal friction method. Although internal frictions for both samples show a reduction when Gd^{3+} content increases, differences have been found between change tendencies of Tg and ΔE_a of GMA-PMMA and GOA-PMMA as the concentration of Gd^{3+} increases. The behaviour of GMA-PMMA is similar to that of PMMA ionomers and the rates of change of T_g with ion concentration are found to be 15.6°C and 18.9°C per mol% of Gd^{3+} content at 0.7 and 0.1 Hz, respectively. A maximum T_g of GOA-PMMA appears at 0.3 mol% concentration of Gd^{3+} and 0.7 Hz.

Explanations have been given in terms of structure differences, plasticization of GOA and interactions between ions and PMMA chains. Based on this, a new model of multiples is given for GOA-PMMA sample: ions are on the out surface of the multiples and long aliphatic chains of GOA composes of the core of the multiplet because they are not compatible with polar matrix of PMMA.

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