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Viscoelasticity of Potassium Neutralized Telechelic Poly(ethylene-butylene) Ionomer in Non-polar Solvent

Syed A. RAHMAN, Akihiko TAKADA*, and Norio NEMOTO

*Department of Molecular and Material Sciences, IGSES,
Kyushu University, Hakozaki, Fukuoka 812-8581, Japan.
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Viscosity and viscoelasticity were measured for potassium neutralized telechelic poly(ethylene-butylene) ionomer, CTPEB-K, as well as the original polymer, CTPEB, in a non-polar solvent of decalin in a concentration range from dilute to semidilute regime. CTPEB-K was found to associate with each other even in the dilution limit. With increasing the polymer concentration, CTPEB-K solution showed a rapid increase in viscosity due to the formation of a huge cluster and further increase in the concentration lead to formation of a viscoelastic network with finite but quite high viscosity. The time-temperature superposition could be applied for the viscoelasticity of the network and the Arrhenius type of temperature dependence was observed. The viscoelastic network exhibited two or three relaxation modes. The fast mode may be assigned to the network rearrangement and the slow mode possibly to the cluster migration in the viscous fluid.

Key Words: Viscoelasticity/ Telechelic ionomer/ Potassium neutralization/ Network rearrangement/ Cluster formation

1. INTRODUCTION

Ionomers are polymers containing small amount of ionic groups onto the nonionic backbone chains. Because the ionic modification induces a drastic improvement of the mechanical properties, the ionomers have attracted a great deal of attention for both their applications and academic interests. Telechelic ionomers are ionomers in which ionic groups are selectively attached at two ends of linear chains. From simplicity of their structures, they are regarded as a model polymer of ionomers and have been extensively studied to elucidate relationships between mechanical properties and association structure of ionomers.¹⁻⁹⁾ Although structures and properties of telechelic ionomers in bulk have been studied extensively, relatively little effort has been made to develop an understanding of their solution behavior.¹⁰⁻²⁴⁾ Especially, there seems to be no report dealing with the association process of ionomers in a wide concentration range from dilute to concentrated regime.

In a previous report, we measured steady viscosity as well as dynamic viscoelasticity of magnesium neutralized telechelic poly(ethylene-butylene) ionomer (CTPEB-Mg) in decalin over the entire polymer concentration range from very dilute state

to the bulk.^{25,26)} Steady state viscosity η increased with polymer concentration C by nearly ten orders of magnitude from an order of 10^{-3} Pa s for C less than 7wt% to 10^7 Pa s in bulk at 298K accompanied by two-steps steep rises at around $C=10$ and 35wt%. The time-temperature and time-concentration scheme were found successful for superposition of the storage and the loss shear moduli against the angular frequency curves. These results were related to changes in solution structures of this system with C taking into account of the divalent nature of the Mg^{2+} ion so that all Mg cations may be present in a non-polar solvent as either in a form of $-COO^-Mg^{2+}-OOC-$ connecting two chain ends or in metal ion clusters at which a number of chains are connected for network formation because charged forms such as $-COO^-$ and $-COO^-Mg^{2+}$ are quite unstable in non-polar solvent.

When a monovalent cations like K^+ ions are used for neutralization, ion pair of COO^-K^+ at chain ends may, in principle, be present even in a non-polar solvent as a strong dipole because the electrically neutral condition is satisfied by the ion pair formation. Associating forms also should be considered such as *pairwise associate* formed by two COO^-K^+ ion pair dipoles and *ion cluster* including many K^+ and COO^- ions. Then it is likely that solution structure as well as their change with polymer concentration for K^+ neutralized CTPEB may be different from those observed for Mg^{2+} neutralized CTPEB.

* To whom correspondence should be addressed.
Phone : +81-92-642-3824, Fax : +81-92-642-3825
e-mail: takada@mm.kyushu-u.ac.jp

In this study, we present the results of steady shear and dynamic viscoelastic measurements on low molecular weight potassium neutralized carboxylate telechelic poly(ethylene-butylene) ionomer (CTPEB-K) in decalin, which were done in a concentration range from dilute to concentrated regime to obtain new information regarding the aggregation behavior of the ionomer in solution and the association process with increasing ionomer concentration. In order to compare the results of CTPEB-K, we also performed viscosity and viscoelasticity measurements for original non-neutralized CTPEB and esterified CTPEB which can not be associated with each other.

2. EXPERIMENTAL

2.1 Materials and sample preparation

Carboxyl terminated poly (ethylene-butylene) copolymer (CTPEB) with low molecular weight ($M_n=1400$) was given by Nippon Soda Co. Ltd.

Esterified CTPEB (CTPEB-Ester) as ethyl carboxylate was prepared by the acylchloride method. 10 times equivalent amount of thionyl chloride to the carboxyl group was added to 5wt% of THF solution of CTPEB. After 1 hour reaction at 25°C, excess amount of thionyl chloride was removed by evaporation. The system was reacted with 10 times equivalent amount of dried ethanol diluted by benzene at 70°C for 48hours. After reaction, all volatile components were evaporated in vacuum at 80°C. Conversion is checked by IR measurements. The absorption peak of acid carbonyl at 1710 cm^{-1} was completely disappeared and alternatively a new absorption peak at 1742 cm^{-1} attributed to acetate carbonyl appeared.

CTPEB-K was prepared by complete neutralization of CTPEB by stoichiometric amount of potassium methoxide in benzene. The solution concentration of CTPEB was adjusted to about 5wt%.

Neutralization was carried out in a distillation apparatus. After five successive evaporations of about 80% amount of benzene and additions of the compensating amount of benzene were done for removal of ethanol, most of benzene was removed by evaporation. Furthermore, the sample was dried in vacuum for several days at 80°C until all benzene were removed. The absorption peak of carboxylic acid at 1710 cm^{-1} was completely disappeared and a new absorption peak at 1560 cm^{-1} assigned to carboxylate appeared.

2.2 Methods

Solution viscosity η of dilute solutions were measured with an Ubbelohde type of capillary viscometer at $25 \pm 0.05^\circ\text{C}$ to obtain intrinsic viscosity $[\eta]$. In rheological measurements, the storage and the loss shear moduli, $G'(\omega)$ and $G''(\omega)$, of the samples were measured in the angular frequency ω range from 0.1 to 100 rad/s at 5 to 55°C to an accuracy of 0.1°C using a stress-controlled rheometer (Carri-MED, CLS-100) with a 4cm cone-plate geometry covered with a humidity chamber to prevent solvent evaporation. The steady shear viscosity was also measured by the rheometer with 6cm cone-plate geometry for intermediated concentration samples.

3. RESULTS AND DISCUSSION

3.1 Viscosity and viscoelasticity of prepolymer samples

Results of viscometric measurements for dilute solutions of CTPEB and CTPEB-Ester solutions in decalin are shown in Fig. 1 in the forms of the reduced viscosity η_{sp}/C and the inherent viscosity $\ln \eta_r/C$ vs. polymer concentration C . For CTPEB-Ester, the reduced viscosity increases linearly with polymer concentration as suggested by the Huggins equation, $\eta_{sp}/C = [\eta] + k'[\eta]^2C$ where $[\eta]$ is the intrinsic viscosity and k' is the Huggins constant. The value of $[\eta]$ obtained is 6.4 cm^3/g , from which the overlapping concentration C^* of the ester has been estimated as $C^* = 1/[\eta]\rho_s$, where ρ_s is the solvent density.

For CTPEB solutions, an upturn of reduced viscosity curve around $C=0.003 \text{ g/cm}^3$ was observed and $[\eta] = 6.7 \pm 0.1$ is a

Fig.1 Concentration dependence of reduced viscosity, η_{sp}/C , and inherent viscosity, $\ln(\eta_r/C)$, for CTPEB, CTPEB-Ester and CTPEB-K solutions in decalin.

little bit larger than $[\eta]$ of CTPEB-Ester, which may be due to association of CTPEB chains by hydrogen bonding since the end groups of this polymer are carboxyl groups.

The dynamic mechanical behavior of the bulk CTPEB was investigated in the temperature range between 5°C and 35°C. The time-temperature reduction was attempted for both the storage (G') and the loss (G'') moduli and found to be valid to obtain composite curves for G' and G'' by a horizontal shift alone as shown in Fig. 2. These curves exhibit a viscous flow in the low frequency region with $G' \sim \omega^2$ and $G'' \sim \omega^1$ and also the occurrence of transition of G' over G'' in the high frequency region.

The shift factor a_T for bulk CTPEB obtained above and for bulk CTPEB-Ester estimated from the viscosity were plotted in the form of $(T-T_r)/\log a_T$ vs $(T-T_r)$ in Fig. 3 and were found to obey the WLF equation

$$\log a_T = -\{C_1(T-T_r)\}/\{C_2+T-T_r\}$$

where C_1 and C_2 are the WLF coefficients and T_r is the reference temperature chosen at 298 K, which means that the thermorheological behaviors of CTPEB and CTPEB-Ester are well described by the free volume concept as expected for usual amorphous polymers.

3.2 Viscosity of CTPEB-K in dilute solution state

Results of viscometric measurements for CTPEB-K dilute solutions are shown in Fig. 1. The reduced viscosity linearly increased with C in the low concentration region. $[\eta]$ was

estimated as 7.5 cm³/g, which is larger than that of either CTPEB-Ester or CTPEB. These results indicate that CTPEB-K chains are associated with each other even at the infinite dilution limit.

We already reported that magnesium neutralized CTPEB (CTPEB-Mg) was also associated with each other in decalin solution.^{25,26)} Because decalin is a non-polar solvent, electrically neutral condition of ions must be satisfied at any time. Magnesium ion is a divalent cation and carboxyl ion is a monovalent anion. For the neutral condition, association of the end groups of CTPEB-Mg should occur in such a way as R-COO-Mg²⁺-OOC-R. On the other hand, potassium ion is a monovalent cation. Thus, even if the end groups of the polymers are not associated with each other, the electrically neutral condition is satisfied for CTPEB-K to form an ion pair such as R-COO-K⁺. However, the results of viscometric measurements strongly suggest that the ion pair aggregates with each other, that is, the ion pair forms pairwise associate and/or ion cluster even in dilute solutions of a non-polar solvent. In order to reveal detailed association structure, the size of the cluster formed by association of polymers must be estimated as well as the intrinsic viscosity. The dynamic light scattering measurement, however, did not afford a reliable value simply because the refractive index of CTPEB is close to that of decalin. It should be noted that the intrinsic viscosity of CTPEB-Mg was lower than that of corresponding CTPEB while the intrinsic viscosity of CTPEB-K was higher than that of CTPEB. This difference must come from difference in the

Fig.2 Time-temperature superposition of storage and loss shear moduli, G' and G'' , for bulk CTPEB sample. Open symbols denote G' and closed symbols denote G'' . The reference temperature is 298 K.

Fig.3 WLF plot of $(T_r - T) / \log a_T$ against $(T - T_r)$ for the shift factor a_T of bulk CTPEB sample. The reference temperature, T_r is 298 K. $(T_r - T) / \log a_T$ for CTPEB-Ester estimated from temperature dependence of viscosity is also plotted. Circles indicate CTPEB data and squares CTPEB-Ester data.

associating structures between CTPEB-K and CTPEB-Mg. Large $[\eta]$ value of CTPEB-K implies that CTPEB-K forms an anisotropic association such as a linear type of association. The simplest model is a linear type of association formed by pairwise associate at chain ends. The necklace type of association observed for several associating polymers could also be considered as a model.^{29,30)} At present, however, we can not determine the association structure. From the value of intrinsic viscosity, the overlapping concentration C^* of CTPEB-K solution was estimated as $C=14\text{wt\%}$.

3.3 Viscosity of CTPEB-K above $C=1\text{wt\%}$

The concentration dependence of viscosity η for CTPEB and CTPEB-K at 25°C is shown in Fig. 4. Viscosities for CTPEB-K solutions with $C>15\text{wt\%}$ were estimated from results of viscoelastic measurement which shall be described later. The viscosity of CTPEB-K solutions is higher than that of CTPEB over the whole concentration range. Below $C=3\text{wt\%}$, the viscosity of CTPEB-K samples is comparatively close to that of CTPEB solutions. The viscosity of CTPEB-K begins to increase much more rapidly than that of CTPEB solutions. The viscosity increases as $\eta \sim C^{4.6 \pm 0.3}$ for $C \geq 15\text{wt\%}$.

As already described, CTPEB-K chains associate with each other in very low concentration. With increasing concentration, the association seems to be accelerated and the size of clusters formed by polymers must become larger and larger. This phenomenon appears similar to the growth of polymer clusters for gel network formation, where the

Fig.4 Concentration dependence of viscosity for CTPEB and CTPEB-K solutions in decalin at 298K. Circles indicate CTPEB data and squares CTPEB-Ester data.

viscosity increases drastically near the sol-gel point because of huge cluster formation and diverges at the sol-gel point. By analogy, the increase in viscosity around $C=7\text{wt\%}$ in this system may be attributed to huge cluster formation by CTPEB-K chains.

The drastic increase in viscosity exhibited above $C=5\text{wt\%}$ did not continue above $C=15\text{wt\%}$ and different concentration dependence was observed for samples with $C \geq 15\text{wt\%}$. Formation of the network extending over the whole system seems to have occurred between 7-15wt%, being close to the overlapping concentration $C^*=14\text{wt\%}$ estimated from $[\eta]$. The network formed above 15wt% can rearrange by recombination of the association points so that the finite viscosity was observed even for high concentration samples.

3.4 Viscoelasticity of CTPEB-K above $C=15\text{wt\%}$

The angular frequency ω dependence of G' and G'' of 20 wt% CTPEB-K sample from $5\sim 55^\circ\text{C}$ are shown in Fig. 5. At 278K, G' takes a plateau value in the high frequency region, which implies that a viscoelastic network is formed in this solution. At elevated temperature of 328K, G'' is larger than G' with $G' \sim \omega^2$ and $G'' \sim \omega^1$ in the low frequency region, which indicates that the solution behaves as a viscous fluid in the long time region.

Fig.5 Angular frequency ω dependence of G' and G'' for 20 wt% CTPEB-K solutions in decalin at 6 temperatures from 278 K to 325 K. For clarity the curves are shifted by 10^n .

The time-temperature superposition principle was found to be applicable for both G' and G'' curves shown in Fig. 5 to obtain one composite curve by a horizontal shift as well as those for the solutions with $C=15, 25$ and 30 wt% as shown in Fig. 6.

The shift factor a_T was not fitted by the WLF equation; no linear relation was observed for a plot of $(T_r - T)/\log a_T$ against $(T - T_r)$. Accordingly the relaxation mechanism does not obey the free volume theory. In Fig. 7, the shift factors for 15~30wt% and the viscosity ratio $T_r \eta(T) / T \eta(T_r)$ for 1~10wt% are semi-logarithmically plotted against $1/T$. Here, for samples with $C=1\sim 10$ wt%, the viscoelastic measurement was not carried out, but if the time-temperature superposition principle were presumably satisfied for these samples, the value of $T_r \eta(T) / T \eta(T_r)$ should take the value same as the corresponding shift factor a_T . Fig. 7 clearly shows that the temperature dependence is well described by the Arrhenius type of equation.

The slope of the lines did not change very much with concentration from 10wt% to 30wt% and the estimated activation energy was found to change from 71 kJmol^{-1} to 80 kJmol^{-1} for 10wt% to 30wt% solutions. Below 10wt%, the slopes for 5wt% and 1wt% samples changed drastically in

Fig.6 Master curves obtain from time-temperature reduction for CTPEB-K solutions in decalin with 4 different concentration from 15wt% to 30wt%. Dotted lines show the curves fitted with the generalized Maxwell model with two relaxation modes for $C=15\sim 25$ wt% and with three relaxation model for $C=30$ wt%.

comparison with those for higher C samples. The estimated activation energies were 19 kJmol^{-1} and 11 kJmol^{-1} , respectively.

This activation energy change means the change in relaxation mechanism of the solutions. At and below 5wt%, the mechanical relaxation should take place by flow of suspension of the clusters formed by association of polymers, where the relaxation is mainly dominated by mobility of the solvent, so that the activation energy observed was fairly small. When cluster size increases and occupation ratio of space by clusters approaches to unity, the relaxation becomes dominated by the rearrangement of the cluster. The sample with $C=10$ wt% exhibited radical extension of viscosity, which should correspond to this situation. At higher concentration exceeding about 12wt%, the transient network will be formed. In this concentration range, the relaxation must be dominated also by the rearrangement process. Activation energy of rearrangement process must be much higher than that of flow of solvent. Therefore, these relaxation processes shows the higher activation energy for 10wt% to 30wt% samples in comparison with the samples with C less than 5wt%.

3.5 Analysis of viscoelasticity by generalized Maxwell model

In Fig. 6, shoulders were obviously observed in G' in the low ω range for all samples, which implies that the presence of a slow relaxation process should be considered for the samples. We attempted to fit the viscoelastic data by a generalized Maxwell model with two relaxation modes.

Fig.7 Semilogarithmic plot of shift factor, a_T , against $1/T$ for CTPEB-K solutions with $C=15\sim 30$ wt%. Viscosity ratio $\{T_r \eta(T) / T \eta(T_r)\}$ is also plotted for CTPEB-K solutions with $C=1\sim 10$ wt%. For clarity the data are shifted by n as indicated.

$$G'(\omega) = \sum_i G_i \tau_i^2 \omega^2 / (1 + \tau_i^2 \omega^2) \quad (1)$$

$$G''(\omega) = \sum_i G_i \tau_i \omega / (1 + \tau_i^2 \omega^2)$$

Here the values of i are 1 and 2 for the two-modes model. τ_1 and τ_2 are relaxation times of the fast and the slow relaxation processes, respectively. G_1 is a plateau modulus for the fast relaxation process and almost corresponds to the plateau modulus observed in Fig. 6. G_2 is a plateau modulus for the slow relaxation process and gives the shoulders of G' in Fig. 6. The fitting by the two-modes model looks quite successful except for the solution with $C=30\text{wt}\%$ as shown in Fig. 6. For $C=30\text{wt}\%$, two-modes fitting was poor. Thus, we tried to fit by the three-modes model with an additional relaxation time τ_3 between τ_1 and τ_2 , which looks quite successful as shown in Fig. 6.

The concentration dependence of τ_1 and τ_2 is shown in Fig. 8, where τ_3 was also plotted for $C=30\text{wt}\%$. τ_2 is greater than τ_1 by two orders of magnitude and the ratio of τ_2 to τ_1 increased with increasing concentration. τ_1 is proportional to $C^{1.1 \pm 0.1}$, while τ_2 proportional to $C^{3.9 \pm 0.2}$. Fig. 9 shows the concentration dependence of G_1 and G_2 , where G_3 was also plotted for $C=30\text{wt}\%$. The value of G_1 is larger than that of G_2 by about four orders of magnitude and the ratio of G_1 to G_2 slightly increased with increasing concentration. G_1 and G_2 are proportional to $C^{3.5 \pm 0.2}$ and $C^{1.8 \pm 0.2}$, respectively. The steady state

viscosity η can be expressed as $\eta = G_1 \tau_1 + G_2 \tau_2$ for the two-modes Maxwell model. From results obtained above, the value of $G_1 \tau_1$ was found to be much larger than $G_2 \tau_2$. Thus, although τ_1 is short, the fast relaxation process dominantly contributes to viscosity of the system. For the result of $C=30\text{wt}\%$ fitted by the three-modes model, $G_1 \tau_1$ is much larger than $G_2 \tau_2 + G_3 \tau_3$ so that the fast relaxation process dominantly contributes as well. In Fig. 4, viscosity above $C=15\text{wt}\%$ has been found to be proportional to $C^{4.6 \pm 0.3}$, which is well described by this argument; $\eta = G_1 \tau_1 + G_2 \tau_2 (+G_3 \tau_3) \approx G_1 \tau_1 \sim C^{4.6}$.

3.6 Fast and medium relaxation processes

Associating polymers form network in solution in high polymer concentration range by formation of crosslinking points (associating points). When the associating points consecutively decompose and regenerate with time, a relaxation process corresponding to the recombination of associating points can be observed.^{27,28)} In the solutions above $C=15\text{wt}\%$, a viscoelastic network should be formed in the system where the fast relaxation process corresponding to G_1 and τ_1 can be attributed to the rearrangement of the network.

As described in the *Introduction*, two types of associating points can be considered. First one is the pairwise associate which is formed by association of two ion pairs of $-\text{COO}^-\text{K}^+$ with a strong dipole moment. Second one is the ion cluster in which many K^+ and $-\text{COO}^-$ ions take part. At the lower range of network formation concentration, network was formed mainly by pairwise associate. In this case, the mechanical relaxation dominantly takes place by the rearrangement of

Fig.8 Concentration dependence of the slow relaxation time, τ_1 , and the fast relaxation time, τ_2 , estimated by fitting with the generalized Maxwell model. τ_3 is also plotted for $C=30\text{wt}\%$.

Fig.9 Concentration dependence of G_1 and G_2 estimated by fitting with the generalized Maxwell model. G_3 is also plotted for $C=30\text{wt}\%$.

Fig.10 Plot of the reduced modulus of G_2 by the form of $G_2 \tau_2 / \pi \eta$ against concentration. A detailed description is written in the text.

pairwise associates even when the rearrangement of ion clusters do not effectively occur. This rearrangement process of pairwise associates should correspond to the fast relaxation process. With increasing the polymer concentration, contribution of ion clusters to form network formation increases. The relaxation process starts to be affected by the rearrangement of ion clusters and distribution of the relaxation process of network should become broader. This effect could bring about a longer relaxation process, i.e. a medium relaxation process observed in $C=30\text{wt}\%$. To obtain detailed information of this longer relaxation process, investigation of solutions with a higher polymer concentration must be needed and is in progress at present.

3.7 Slow relaxation process

At present, it is difficult to determine what process is attributed to the slow relaxation process definitely. One of the possibilities is the migration of polymer clusters. In this system, network is formed by virtue of two types of association as described above. In the time region shorter than the time for associating points to recombine, network structure does not change. On the other hand, in the time region longer than the time for recombination of pairwise associate, network structure changes with time and the system can flow by rearrangement of the network. Even in this long time region when the system can flow, polymer clusters formed by ion clusters keep its structure and polymers in the cluster collectively move in this system in this time region before the recombination process of ion clusters occurs. Therefore, these polymer clusters can invoke an additional relaxation process similar to that of suspensions of microspheres.

The relaxation of suspensions essentially comes from Brownian motion of microspheres.³¹⁾ The characteristic time is

estimated by $\tau_B = a^2/6D$ where a is a radius of the sphere and D is the diffusion coefficient of the sphere. D is related to the radius a and solvent viscosity η by the Stokes-Einstein relation $D=kT/6\pi\eta a$ in dilute condition. Therefore,

$$\tau_B = \pi\eta a^3/kT \quad (2)$$

is obtained. When the viscosity at the high frequency limit, η_∞ , i.e., the viscosity observed at frequency higher than the characteristic time, is used instead of η in eq. (2), we can measure the mechanical relaxation time, τ_M , by viscoelastic measurement as about half of τ_B at the volume fraction ϕ lower than 0.5.³¹⁾

$$\tau_M = \tau_B/2 = \pi\eta_\infty a^3/2kT \quad (3)$$

In our system, η_∞ takes almost the same value as η estimated in the long time region, because G'' is almost a straight line with the slope of unity around $\omega=1/\tau_2$.

The polymer cluster actually has a size distribution and its shape must not be an ideal sphere. If we ignore these effects for simplicity, we can apply eq. (3) for τ_2 . The estimated values of a for samples with $C=15\text{wt}\%$ to $30\text{wt}\%$ are ranged from 28nm to 25nm. As already estimated, the intrinsic viscosity for CTPEB-Ester is $6.4\text{cm}^3/\text{g}$. If this value can be regarded approximately as to correspond to the dimension of PEB main chain due to the non-associating nature of CTPEB-Ester, we can roughly estimate the diameter of a single chain of PEB as about 3nm. Using this value as a diameter of the occupied volume for a CTPEB single chain, the diameter of cluster is almost 8-9 times as large as that of a single chain. As the polymer cluster should not be rigid but soft and does not have an ideal spherical shape, this obtained value should be regarded as an effective radius. This result, however, suggests that the associated cluster may consist of hundreds or thousands of CTPEB polymer chains.

Modulus of suspension with low concentration, G , can be estimated by $G=(n/V)kT$, where n is the number of particles in the system, V the volume of this system. Using volume fraction, ϕ , expressed by $\phi=(4/3)\pi a^3 n/V$ where a is a radius of the particle, G is expressed in the form of reduced modulus Ga^3/kT by $Ga^3/kT=(3/4\pi)\phi$. The general expression for higher concentration is

$$Ga^3/kT = (3/4\pi)\phi + k_2\phi^2 + k_3\phi^3 \dots \quad (4)$$

When we substitute a^3 using eq. (3), and G_2 , τ_2 and η are used as G , τ_M and η_∞ , respectively, we can estimate Ga^3/kT by

$$Ga^3/kT = 2G\tau_M/\pi\eta_\infty = 2G_2\tau_2/\pi\eta \quad (5)$$

Fig. 10 shows the plot of $G_2\tau_2/\pi\eta$ against the polymer concentration. Linear relation between $G_2\tau_2/\pi\eta$ and C are apparently satisfied, which may imply that volume fraction of polymer cluster formed by ion clusters, ϕ , is proportional to polymer concentration, C , and the higher term of eq. (4) can be neglected. Two reasons may be considered for the omission of higher terms. One of the reasons is a small value of ϕ . We can estimate $\phi=0.067$ for $C=30\text{wt\%}$ using the eq.(4) without higher terms. Another reason is the nature of the cluster with soft boundary. Eq. (4) is essentially applied to systems of hard spheres. The estimated value is effective one so that a true volume fraction covered by polymer cluster may be much larger than the calculated value. However, even if large volume is occupied, only first term might contribute to the modulus in the case of clusters with soft boundary.

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