



Influence of the concentration of lanthanum on the dynamics of poly (methyl methacrylate-co-lanthanum methacrylate) ionomers



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Introduction

Ionomers are nominally random copolymers that consist of a hydrocarbon backbone and a relatively small fraction (ca.<10%) of pendent groups with acid functionality, neutralized partially or completely with cations. Because of the aggregation of ionic species into clusters, which serve as physical cross-links, there are profound effects on thermal, mechanical, and charge transport properties.¹

Although ion aggregations and properties of ionomers have been studied using a number of different techniques, little is known about the effect of these ionic clusters on the molecular dynamics of this class of materials.² Broadband dielectric relaxation spectroscopy is powerful tool for understanding the influence of ions on segmental and local motions as well as aggregate dynamics.¹

Among most of research on the ionomers, they focus on the monovalent and/or bivalent counterions and rarely pay attention to multivalent counterions. In this investigation, the authors chose poly (methyl methacrylate-co-methylacrylic acid) as matrix and lanthanum as counterion to discuss the correlation between ionic aggregate structure and chain dynamic.

Theory

The dielectric relaxation parameters related to the chain dynamic were obtained by fitting the isothermal dielectric loss ϵ'' curves with the Havriliak-Negami (HN) function:

$$\epsilon^* = \epsilon_\infty + \frac{\Delta\epsilon}{[1 + (i\omega\tau_{HN})^{\alpha_{HN}}]^{\beta_{HN}}} - i \frac{\sigma}{\epsilon_0\omega^s}$$

in which ϵ^* is the complex dielectric permittivity; the dielectric strength $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$, where ϵ_∞ and ϵ_0 are the dielectric constants at limiting high and low frequencies, respectively; ω is angular frequency; τ_{HN} is the characteristic relaxation time; α_{HN} and β_{HN} are relaxation shape parameters, indicative of the breadth of the relaxation and peak asymmetry (in log form), respectively; σ is the dc conductivity; s characterizes the nature of the conduction process.

The characteristic relaxation time is related to the time of maximum loss by

$$\tau_{max} = \tau_{HN} \left(\sin \frac{\alpha_{HN} \beta_{HN} \pi}{2(\beta_{HN} + 1)} \right)^{1/\alpha_{HN}} \left(\sin \frac{\alpha_{HN} \pi}{2(\beta_{HN} + 1)} \right)^{-1/\alpha_{HN}}$$

and the maximum relaxation time follows a Vogel-Fulcher-Tammann (VFT) equation:

$$\tau_{max} = \tau_0 \exp\left(\frac{B}{T - T_0}\right)$$

in which τ_0 and B are constant, τ_0 is sometimes associated with vibration lifetimes, B is related to the apparent activation energy, and T_0 is the Vogel temperature.

In order to eliminate the contribution of the dc conduction on ϵ'' in high temperature, we chose an ohmic-conduction-free loss that is determined from the logarithmic derivative of the dielectric constant:

$$\epsilon''_D = -\frac{\pi}{2} \frac{\partial \epsilon'(\omega)}{\partial \ln \omega}$$

Materials and Methods

Poly (methyl methacrylate) (PMMA) was partially hydrolyzed to acid form and the acid content was determined as 3.50mol% by titration. The acidified PMMA, named PMMH, was refluxing with an ethanol solution of sodium acetate/LaCl₃(molar ratio of 3:1) to get a series of ionomers with variable contents of La ion. The La content was determined using inductively coupled plasma atomic emission spectrometry. Based on the neutralization of the acid, the samples were named as 30%, 60%, 90%, 100%, 150%, 200%, respectively.

Table 1 the contents of La in samples

Sample	30%	60%	90%	100%	150%	200%
Ion content (mmol/g)	0.0315	0.0804	0.107	0.119	0.183	0.263

Results and Discussions

1. β relaxation

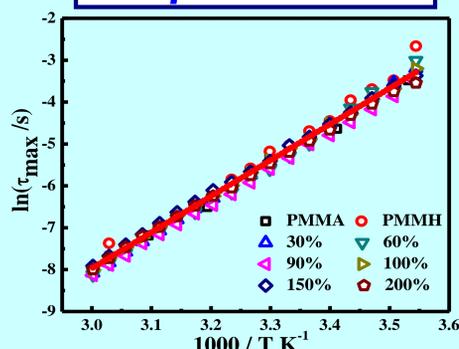


Figure 1. Temperature dependence of the relaxation times for the β processes of PMMA, PMMH and La-ionomers. The dotted line represents the Arrhenius fit.

As seen in Figure 1, the β processes exhibit the Arrhenius behavior, with the same activation energy about 72 kJ/mol for all samples regardless of the increasing of the La ions, which is because the molecular mechanism of β process is due to the hindered rotation of the $-\text{COOCH}_3$ group about the C-C bond.

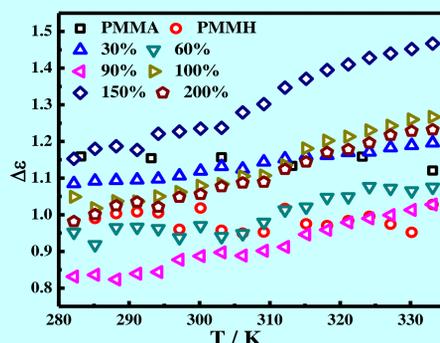


Figure 2. Temperature dependence of the dielectric relaxation strengths for the β processes of PMMA, PMMH and La-ionomers.

It shows in Figure 2 that relaxation strengths increase slightly with temperature for all samples due to greater dipole mobility at high temperature.

2. α relaxation

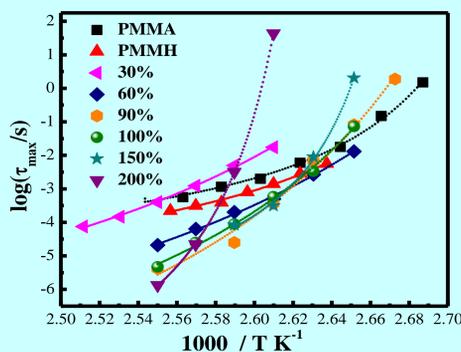


Figure 3. Temperature dependence of the relaxation times for the α processes of PMMA, PMMH and La-ionomers. The dashed lines represent the VFT fittings.

Table 2 T_{gs} and relevant fitting parameters of the VFT equation for PMMA, PMMH and La-ionomers.

Sample	log τ_0	B	T ₀ (K)	T _{ref} (K)	T _{DSC} (K)	T _{DMA} (K)
PMMA	-5.374	64.548	360.60	369.35	363	388
PMMH	-6.291	87.842	357.502	368.10	373	390
30	-10.188	314.750	345.93	371.35	376	401
60	-11.710	376.184	338.87	366.31	374	392
90	-13.636	343.617	349.60	371.58	378	395
100	-11.918	264.360	352.52	371.51	377	394
150	-7.317	48.861	370.75	375.99	377	395
200	-11.054	78.251	376.99	382.98	378	398

Figure 3 shows the maximum relaxation times of segmental processes that fitted with VFT equation and the relevant parameters are presented in table 2. From the parameters, it is known that the fragility of the material is decreasing with the increasing of La ions, which is due to the cross-links of ion aggregation. When the neutralization increases to more than 150%, the fragility increase. It may be because that the ions aggregate to clusters.

3. High temperature processes

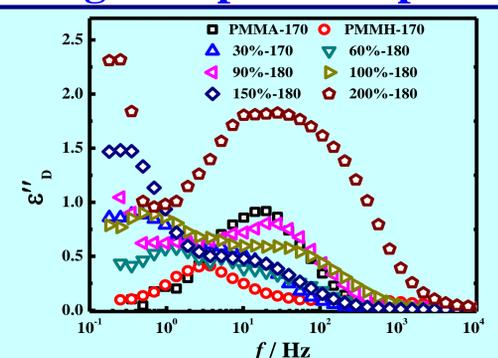


Figure 4. Dielectric loss spectra vs frequency of the high temperature processes for PMMA, PMMH and La-ionomers.

Two well-defined processes are observed in the low frequency region as shown in the Figure 4. There are several possible origins of these processes such as Maxwell-Wagner-Sillars (MWS) interfacial polarization, electrode polarization (EP) and α^* process involving ion aggregations.

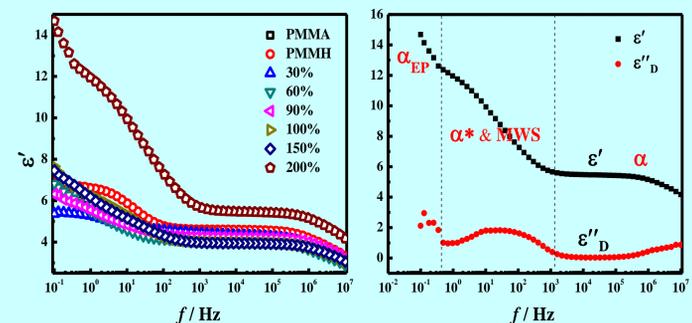


Figure 5. Frequency dependence of the dielectric constants of PMMA, PMMH and La-ionomers.

From the Figure 5, it is known that the two processes displayed in Figure 4 are MWS interfacial polarization and α^* process. For EP process, there is a very large increase (generally exponential change) in dielectric constant at low frequency.

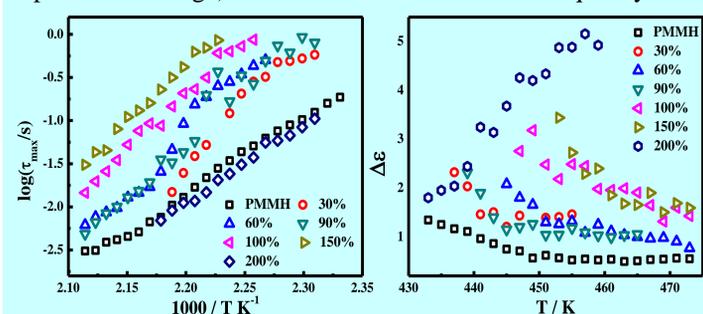


Figure 6. Temperature dependence of the relaxation time and dielectric relaxation strengths for the α^* processes of PMMH and La-ionomers.

Figure 6 presents the relaxation times and dielectric strengths of α^* process of PMMH and La-ionomers. The relaxation times do not accord with Arrhenius equation or VFT equation and seemingly present a three-section relaxation behavior. The dielectric strengths also display different trends in high ion contents. These phenomenon need further studied.

conclusion

The dynamics of PMMA, PMMH and La-ionomers were investigated by using broadband dielectric relaxation spectroscopy. Four well-defined processes were observed in the range of test frequency. β process is due to the hindered rotation of the $-\text{COOCH}_3$ group about the C-C bond and not affected by increasing ion contents. The fragility decreased at first and increased later because of the ion aggregating from multiplets to clusters. And the α^* process involving the ion aggregations is found and presents some different relaxation behavior.

Reference

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