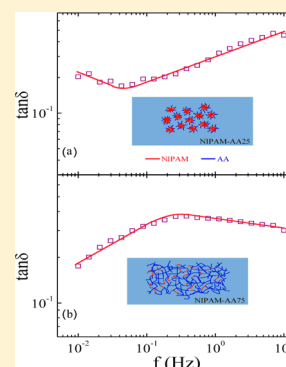


Dynamics in *N*-Isopropylacrylamide-acrylic Acid Copolymer Aqueous Solution from Mechanical Spectroscopy

Huagang Wang,[†] Xuebang Wu,^{*,†} C. S. Liu,^{*,†} Zhengang Zhu,[†] Zhuo Ao,[‡] and Guangzhao Zhang[‡][†]Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, P.O. Box 1129, Hefei, Anhui, People's Republic of China[‡]Hefei National Laboratory for Physical Sciences at the Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei, P. R. China 230026

ABSTRACT: Gaining control over precise and predictable structures of colloidal systems and understanding the abundant dynamic behaviors remains a formidable challenge. In this study, low-frequency mechanical spectroscopy was applied to investigate the dynamics of aqueous solutions of *N*-isopropylacrylamide-acrylic acid (NIPAM-AA) copolymers with three different AA contents. A mechanical loss valley was found for the solution with low molar fraction of AA (f_{AA}), $f_{AA} = 25$ and 50 mol %, and a loss peak was shown for the solution with $f_{AA} = 75$ mol %. The former is suggested to be due to the particle glass phase of repulsive micelles above the low critical solution temperature, whereas the latter is associated with the α relaxation behavior of NIPAM-AA/water mixture at high concentrations. The relaxation time of the α relaxation seems to follow a simple Arrhenius temperature dependence. The activation energy H is ~ 53 kJ/mol, and the larger H value is suggested to be due to multiple strong hydrogen bonds in the copolymer solution. The present work demonstrates that by controlling the proportion of ingredients in the colloidal systems the systems can exhibit distinct dynamic behaviors, which is helpful in the design and fabrication of colloids.



INTRODUCTION

Poly (*N*-isopropylacrylamide) (PNIPAM), which exhibits a low critical solution temperature (LCST) at ~ 33 °C, has received great attention in past years due to its abundant biomedical applications.¹ With copolymerization of other hydrophobic or hydrophilic monomers, the LCST and phase behavior can be changed greatly.^{2,3} A soft colloidal system that is commonly used is copolymerized from *N*-isopropylacrylamide (NIPAM) and acrylic acid (AA), resulting in NIPAM-AA segmented copolymer or microgels. These systems have physical and chemical behaviors that are sensitive to pH, ionic strength, temperature, and polymer content.^{4–6} Up to now, various techniques such as differential scanning calorimetry (DSC) and light scattering have been employed to examine the phase behaviors of the NIPAM-AA copolymer, especially the mechanism of the LCST behavior.^{2,7,8} However, little research focuses on the dynamics of concentrated copolymer solutions, especially with high content of AA, which is the subject of the present study.

On the other hand, a remarkable characteristic feature of disordered dense systems such as concentrated polymer solutions or colloidal suspensions is their relaxation behaviors. Dynamics of these systems has received considerable experimental and theoretical interest not only from a fundamental point of view but also for technological applications.^{9–12} In general, the dynamic of the primary (α) relaxation often shows non-Arrhenius behavior, and the spectral shapes are found to be strongly non-Debye and phenomenologically described in terms of the Kohlrausch–Williams–Watts

(KWW) relaxation function.^{13–15} Linear response experiments are usually reported in terms of the frequency dependence of the rheological quantities.^{15–17} In this article, by using mechanical spectroscopy, we have investigated the dynamics of concentrated NIPAM-AA copolymer aqueous solutions with three molar fraction of AA (f_{AA}). Through the frequency response experiments, a mechanical loss valley is found for the copolymer solutions with $f_{AA} = 25$ and 50 mol %, which is due to the repulsive micelle glass phase above the LCST. Moreover, a mechanical loss peak is shown for the copolymer solution with $f_{AA} = 75$ mol %, which is related to the α relaxation behavior of NIPAM-AA chains in water.

EXPERIMENTAL SECTION

N-Isopropylacrylamide was recrystallized three times in a benzene/*n*-hexane mixture. AA from Aldrich and azobis-(isobutyronitrile) (AIBN) from Acros were recrystallized three times from methanol. The polymerization of NIPAM (111 mM) and AA (46.1, 92.2, and 138.3 mM) in deionized water was conducted in a 100 mL three-necked flask under a N_2 atmosphere at 70 °C using AIBN (0.37 mM) as the initiator. The solvents were removed by freeze-drying, and the copolymers were redissolved in deionized water. The aqueous solutions were further purified by dialysis by using a semipermeable membrane with a cutoff molar mass of 5000

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g/mol. The resulting molar fraction values of AA determined by titrating the copolymer solution in water with a sodium hydroxide solution under a N_2 blanket at 25 °C were 25, 50, and 75 mol %. They are designated as NIPAM-AA25, NIPAM-AA50, and NIPAM-AA75. The desired concentrated aqueous solutions of NIPAM-AA copolymer were then prepared by dissolving the copolymer in deionized water and kept at 5 °C for several days before being used.

The mechanical spectroscopy measurements of the linear viscoelastic properties of the solutions were performed on our internally built torsion apparatus. Such measurements were conducted on a modified low-frequency inverted torsion pendulum with a Couette-like setup using the forced-vibration method. A water bath was used to control the temperature within 0.1 °C. The details of the device can be found elsewhere.¹⁸ In the measurement, the inner cup is forced into torsional vibration by a time-dependent force $F(t) = F(0) \sin(\omega t)$, where ω is the circular frequency ($= 2\pi f$, f is the measuring frequency). The angular displacement function of the cup, $A(t) = A(0) \sin(\omega t - \delta)$, is measured optically, where δ is the phase difference between $F(t)$ and $A(t)$. The loss tangent $\tan \delta$ and the relative modulus $G = F(0)/A(0)$ were measured as functions of temperature or frequency. The nonisothermal measurements were performed with a fixed frequency and applied stress, and the heating rate is 1/6 °C/min to ensure the quasistatic test from 10 to 50 °C. In the isothermal measurement, the measurements were carried out in a frequency range of 0.01 to 10 Hz. For all samples, the mechanical measurements were taken after 5 min preshear at 2 Hz.

RESULTS AND DISCUSSION

The loss tangent, $\tan \delta$, is an alternative to the storage modulus G' and loss modulus G'' to characterize the viscoelastic properties of polymer. It is known that $\tan \delta$ is related to the energy dissipation of the materials, and so the material with a higher damping capability displays a large $\tan \delta$ value. The maximum of $\tan \delta$ with temperature is usually considered to be related to a relaxation process or a phase transition.^{19–22} Figure 1a,b shows the temperature dependences of $\tan \delta$ and relative

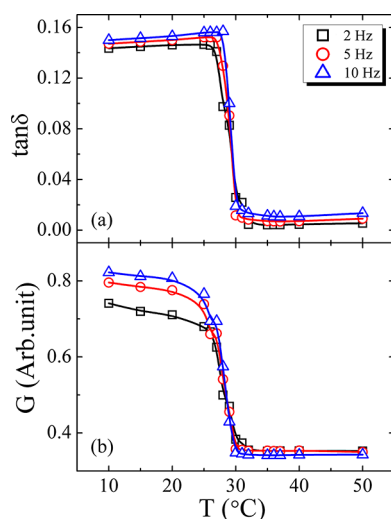


Figure 1. Loss tangent $\tan \delta$ (a) and relative modulus G (b) of NIPAM-AA25 copolymer solution as a function of temperature at copolymer weight fraction $\phi = 0.3$, where $f = 2, 5$, and 10 Hz.

modulus G of NIPAM-AA25 copolymer solutions at $f = 2, 5$, and 10 Hz, where the copolymer weight fraction $\phi = 0.3$. The value of $\tan \delta$ shows an abrupt drop when the temperature reaches ~ 30 °C. Meanwhile, G exhibits a gradual decrease at first and then shows an abrupt drop at ~ 30 °C. The sudden change of $\tan \delta$ and G indicates that the mixture undergoes a structural transition rather than a thermally activated relaxation process because both of them do not depend on the frequencies.^{18,21,22} Because the structure of poly(acrylic acid) (PAA) does not change in the temperature range of 10 to 50 °C,²³ the drastic decrease in $\tan \delta$ and G is caused by the increasing free volume of the system due to the collapse of PNIPAM chains,^{24–26} leading to a transition from a solidlike behavior to a liquidlike behavior. The presence of micelles with PNIPAM forming the micellar core and PAA forming the corona above the LCST of PNIPAM is suggested.²⁷ Because of the outstretched PAA chains on the surface of the micelles, it is expected that the repulsive interaction between the micelles above the LCST, in contrast with the behaviors of PNIPAM microgels,²⁸ leads to a small $\tan \delta$ at low concentration.

Figure 2a,b shows the effect of the concentration of NIPAM-AA25 copolymer solution on $\tan \delta$ and G at $f = 2$ Hz, where ϕ

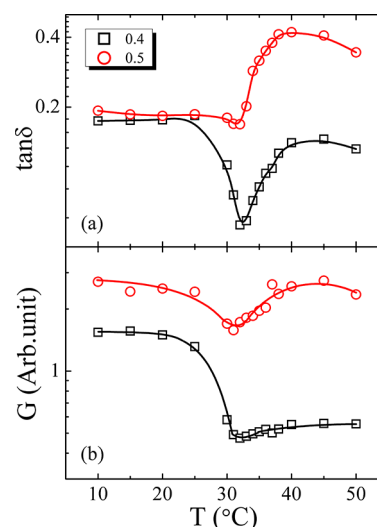


Figure 2. Loss tangent $\tan \delta$ (a) and G (b) spectra of NIPAM-AA25 copolymer solution at 2 Hz, where $\phi = 0.4$ and 0.5.

$= 0.4$ and 0.5. The solutions with different ϕ show a similar variation trend with increasing temperature. However, $\tan \delta$ and G show a large value at a higher ϕ . This is understandable because the greater overlapping and aggregation of micelles at a higher concentration lead the values of $\tan \delta$ and G to increase.

The variation of $\tan \delta$ and G versus temperature for the copolymer solutions with three f_{AA} at $\phi = 0.2$ is plotted in Figure 3. For NIPAM-AA25 and NIPAM-AA50 copolymer solutions, abrupt decreases in $\tan \delta$ and G are observed with increasing temperature, and the change occurs at lower temperature for the copolymer solution with a higher f_{AA} . This indicates a decreasing LCST of the copolymer at a high f_{AA} content, which is consistent with the results of the NIPAM-AA hydrogel.^{25,29} It is expected that the hydrophilization of PNIPAM chain by conjugation with more hydrophilic PAA should result in an increase in the LCST of PNIPAM.^{2,30,31} However, it is quite opposite to the present result, and such difference is also found in the complexes of PNIPAM with

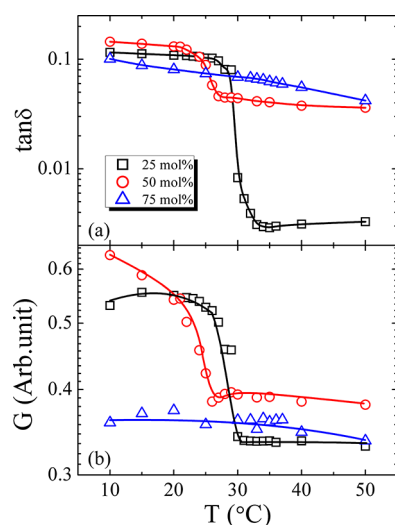


Figure 3. Loss tangent $\tan \delta$ (a) and G (b) spectra for different molar fraction of AA solutions at $f = 2$ Hz and $\phi = 0.2$.

poly(methacrylic acid) (PMA).⁸ A possible explanation is the destruction of the hydrophobic hydration layer around the isopropyl groups of PNIPAM as a result of PAA or PMA binding.⁸ We attribute the decrease in the LCST to the increasing component of PAA that competes with the PNIPAM for water molecules and effectively dehydrates them, promoting hydrophobic segment–segment interaction. As f_{AA} is raised up to 75 mol %, the LCST behavior is hard to be found because both $\tan \delta$ and G show only a slight decrease in the whole temperature range. It is worthwhile to note that the relative reduction of $\tan \delta$ is decreased with increasing f_{AA} because the solubility of more PAA offsets the temperature-sensitivity of PNIPAM components.³²

To characterize the phase behaviors of the solutions, we analyzed the relaxation dynamics by the frequency dependence of the rheological quantities. Because the significant change in different f_{AA} copolymers occurs at high temperature, more attention is paid to the behavior above the LCST. In Figure 4, the loss tangent $\tan \delta$ of NIPAM-AA25 and NIPAM-AA75 copolymer solutions at $\phi = 0.5$ is plotted as a function of frequency on a log–log scale at 50 °C. Distinct behaviors are observed for the two solutions. For NIPAM-AA25 solution, the presence of the minimum in $\tan \delta$ is observed, which is a feature of glassy materials.^{33,34} As mentioned above, upon heating, the dehydration of the PNIPAM chains takes place and the micellization begins. The micelles behave like hard-sphere particles due to the repulsive interaction between the hydration of PAA. With increasing the number of micelles, the motion of micelles is gradually restricted and at last can only rattle within a cage formed by its neighboring particles. The observed increase in $\tan \delta$ with decreasing frequency is suggested to be caused by additional energy dissipation produced by a particle escaping from the cage formed by the neighboring particles.³³ However, for NIPAM-AA75 sample, the response is changed due to the structure change of the system, where the micellization might be restricted because the dominant component of the system turns to the AA segments.

Figure 5a shows frequency-dependent loss tangent spectra of NIPAM-AA75 with three concentrations at 40 °C. The frequency at which $\tan \delta$ takes the maximum value shifts to higher frequency with decreasing concentration, signifying the increasing mobility of chains at higher content of the water.²²

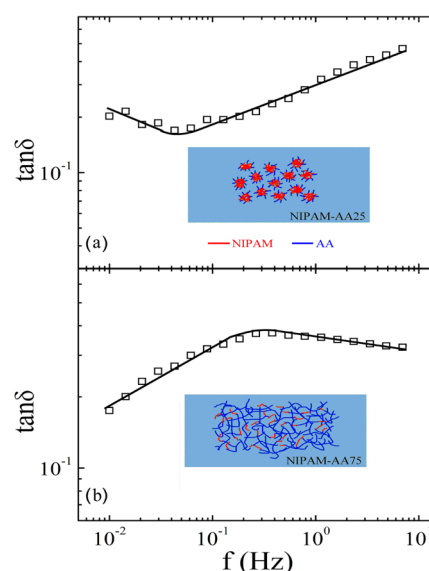


Figure 4. Frequency dependences of $\tan \delta$ for NIPAM-AA25 (a) and NIPAM-AA75 (b) copolymer solutions at $T = 50$ °C and $\phi = 0.5$. The cartoon illustration of the morphology is shown in the relevant copolymer.

The water effectively increases the distance between adjacent main chains of NIPAM-AA, leading to the increase in the mean size of local free volume. Thus, the water plays a plasticizer-like effect. This is reminiscent of the behavior of PAA/water mixtures, where the glass transition can be found at this temperature range and the water, as a plasticizer, decreases the glass-transition temperature of PAA.^{35,36} Because the temperature range of $\tan \delta$ peak agrees well with the glass-transition temperatures of PAA/water mixtures by stepscan DSC measurements,³⁶ the observed $\tan \delta$ peak is most likely related to the α relaxation behavior of the NIPAM-AA chains under the influence of water.

To get a further insight into the relaxation dynamics of the α relaxation of NIPAM-AA/water mixture, we consider the temperature-dependent frequency response of the rheological quantities. Figure 5b shows the frequency-domain $\tan \delta$ spectra of NIPAM-AA75 copolymer solution at $\phi = 0.5$, where $T = 10, 20, 30, 40$, and 50 °C. Note that the $\tan \delta$ peak shifts to high frequencies with increasing temperatures. Moreover, the peak magnitude increases with increasing temperature. The increase in the free volume due to the collapse of the NIPAM segments at higher temperatures may lead to a increasing concentration of mobile species at the relaxation, resulting in a slight enhancement of relaxation strength reflected by the peak magnitude.³⁷ A normalized master curve of the $\tan \delta$ peak is plotted in Figure 5c. It can be seen that the relaxation peak is asymmetric and the width of the peak is much broader than that for classical Debye response, which indicates a broader relaxation time distribution of the system. A slight change among the normalized dissipation peaks at different temperatures is also observed, indicating that the relaxation time distribution is not apparently affected by the temperature. The deviation of high-frequency wing of loss peak may be related to the presence of a faster secondary process at higher frequencies.^{38–40}

For a relaxation process, the relaxation time τ generally follows the Arrhenius law

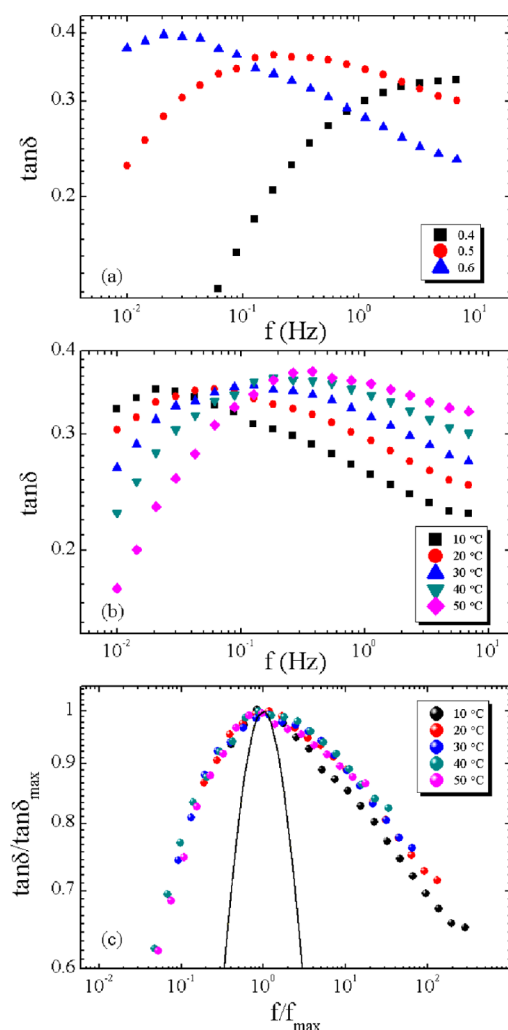


Figure 5. (a) Frequency dependences of $\tan \delta$ for NIPAM-AA75 copolymer solution at 50 °C for different f_{AA} . (b) Mechanical relaxation behavior of NIPAM-AA75 copolymer solution at $\phi = 0.5$ for different temperatures. (c) Normalized master curve for NIPAM-AA75 copolymer solution at $\phi = 0.5$. The solid line represents the standard Debye peak.

$$\tau = \tau_0 \exp(H/k_B T) \quad (1)$$

where τ_0 is the pre-exponential factor (or the relaxation time at infinite temperature), H denotes the activation energy of the relaxation process, and k_B is the Boltzmann constant. It is well known that at the peak position the condition $\omega_p \tau_p = 1$ is fulfilled,⁴¹ where the subscript p denotes the values at peak position. Therefore, the relaxation parameters H and τ_0 can be determined from the temperature-dependent mechanical spectra at different frequencies or from the frequency-domain spectra at different temperatures. If we plot $\ln \tau$ as a function of the reciprocal of peak temperature (Arrhenius plot), a linear relation would be obtained according to eq 1. The so-called Arrhenius plot for the relaxation process of NIPAM-AA75 copolymer solutions at $\phi = 0.5$ is shown in Figure 6, where the solid line is the linear least-squares fitting. The relaxation parameter $H \approx 53$ kJ/mol and $\tau_0 \approx 10^{-9}$ s for the $\tan \delta$ peak are obtained from the fitting line. It should be mentioned that the temperature range is relative narrow (only 40 °C), over which the α relaxation of NIPAM-AA/water mixture occurs, and so

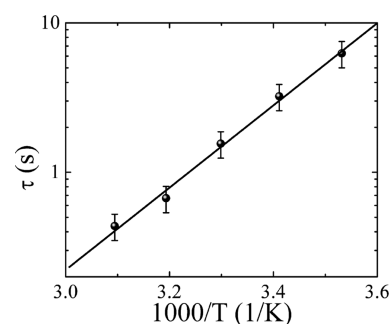


Figure 6. Temperature dependence of the relaxation time of α relaxation for NIPAM-AA/water solution. The solid line is the linear least-squares Arrhenius fitting curve.

the simple Arrhenius behavior of the relaxation time needs to be further studied and proven.

Here the longer τ_0 is reasonable because here the relaxing units are chain segments and their movement needs a longer time than that of atoms ($\sim 10^{-12}$ s) in metals. As described above, the water interacts with PAA chains through strong hydrogen bonding,³⁶ and so the larger H value is suggested to be due to multiple hydrogen bonds in the copolymer solution. Similar results were also observed in liquid hydrogen fluoride and water system and in borate-ion-mediated H-bonding poly(vinyl alcohol) gels.^{42,43} The α relaxation is directly related to the dynamic organization of the hydrogen bonds network of the system, where the activation energy depends on the strength and number of the hydrogen bonds.⁴² In borate-ion-mediated H-bonding poly(vinyl alcohol) gels, the activation energy necessary for dissociation is ~ 30 kJ/mol,⁴³ where the high activation energy is attributed to the multiple hydrogen bonds in the system.⁴⁴ Therefore, the multiple strong hydrogen bonds between water and PAA chains are responsible for the larger activation energy of the α relaxation.

CONCLUSION

The dynamics of NIPAM-AA copolymer aqueous solution with three contents of AA ($f_{AA} = 25, 50$, and 75 mol %) have been investigated by low-frequency mechanical spectroscopy. The LCST behavior of the copolymer could be detected by the evolution of the loss tangent and relative modulus as the temperature is increased at a fixed frequency. For NIPAM-AA25 and NIPAM-AA50 copolymer, a mechanical loss valley is found, which is due to the glass behavior of the micelles above the LCST. For NIPAM-AA75 solution, a relaxation peak is shown, which is associated with the α relaxation of NIPAM-AA chains. The relaxation time of α relaxation seems to follow a simple Arrhenius temperature dependence with an activation energy of ~ 53 kJ/mol.

AUTHOR INFORMATION

Corresponding Author

*Tel: 86-551-5591062. E-mail: xbwu@issp.ac.cn; csliu@issp.ac.cn.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Guan, Y.; Zhang, Y. J. *Soft Matter* **2011**, *7*, 6375–6384.
- (2) Qiu, X. P.; Kwan, C. M. S.; Wu, C. *Macromolecules* **1997**, *30*, 6090–6094.
- (3) Chen, H. W.; Li, J. F.; Ding, Y. W.; Zhang, G. Z.; Zhang, Q. J.; Wu, C. *Macromolecules* **2005**, *38*, 4403–4408.
- (4) Muluneh, M.; Sprakel, J.; Wyss, H. M.; Mattsson, J.; Weitz, D. A. *J. Phys.: Condens. Matter* **2011**, *23*, 1–10.
- (5) Cho, J. K.; Meng, Z. Y.; Lyon, L. A.; Breedveld, V. *Soft Matter* **2009**, *5*, 3599–3602.
- (6) Snowden, M. J.; Chowdhry, B. Z.; Vincent, B.; Morris, G. E. *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 5013–5016.
- (7) Weng, Y. M.; Ding, Y. W.; Zhang, G. Z. *J. Phys. Chem. B* **2006**, *110*, 11813–11817.
- (8) Burova, T. V.; Grinberg, N. V.; Grinberg, V. Y.; Kalinina, E. V.; Lozinsky, V. I.; Aseyev, V. O.; Holappa, S.; Tenhu, H.; Khokhlov, A. R. *Macromolecules* **2005**, *38*, 1292–1299.
- (9) Pochylski, M.; Aliotta, F.; Ponterio, R. C.; Saija, F.; Gapinski, J. *J. Phys. Chem. B* **2010**, *114*, 1614–1620.
- (10) Tassieri, M.; Evans, R. M. L.; Barbu-Tudoran, L.; Khaname, G. N.; Trinick, J.; Waigh, T. A. *Phys. Rev. Lett.* **2008**, *101*, 198301.
- (11) Laurati, M.; Petekidis, G.; Koumakis, N.; Cardinaux, F.; Schofield, A. B.; Brader, J. M.; Fuchs, M.; Egelhaaf, S. U. *J. Chem. Phys.* **2009**, *130*, 134907.
- (12) Erwin, B. M.; Cloitre, M.; Gauthier, M.; Vlassopoulos, D. *Soft Matter* **2010**, *6*, 2825–2833.
- (13) Katana, G.; Fischer, E. W.; Hack, T.; Abetz, V.; Kremer, F. *Macromolecules* **1995**, *28*, 2714–2722.
- (14) Lunkenheimer, P.; Loidl, A. *Chem. Phys.* **2002**, *284*, 205–219.
- (15) Fragiadakis, D.; Roland, C. M.; Casalini, R. *J. Chem. Phys.* **2010**, *132*, 144505.
- (16) Mason, T. G.; Weitz, D. A. *Phys. Rev. Lett.* **1995**, *74*, 1250–1253.
- (17) Wyss, H.; Miyazaki, K.; Mattsson, J.; Hu, Z.; Reichman, D.; Weitz, D. *Phys. Rev. Lett.* **2007**, *98*, 238303.
- (18) Wu, X. B.; Xu, Q. L.; Shui, J. P.; Zhu, Z. G. *Rev. Sci. Instrum.* **2008**, *79*, 126105.
- (19) Wu, X.; Wang, H.; Liu, C.; Zhu, Z. *Soft Matter* **2011**, *7*, 579.
- (20) Wu, X.; Shang, S.; Xu, Q.; Liu, C.; Zhu, Z.; Zhang, G. *Appl. Phys. Lett.* **2008**, *93*, 011910.
- (21) Wu, X. B.; Zhu, Z. G.; Shang, S. Y.; Xu, Q. L.; Shui, J. P.; Zhang, G. Z. *J. Phys.: Condens. Matter* **2007**, *19*, 466102.
- (22) Zhou, X. M.; Wu, X. B.; Wang, H. G.; Liu, C. S.; Zhu, Z. G. *Phys. Rev. E* **2011**, *83*, 041801.
- (23) Chen, G. H.; Hoffman, A. S. *Macromol. Rapid Commun.* **1995**, *16*, 175–182.
- (24) Ikkai, F.; Suzuki, T.; Karino, T.; Shibayama, M. *Macromolecules* **2007**, *40*, 1140–1146.
- (25) Kishi, R.; Kihara, H.; Miura, T. *Colloid Polym. Sci.* **2004**, *283*, 133–138.
- (26) Zhang, X. Z.; Yang, Y. Y.; Wang, F. J.; Chung, T. S. *Langmuir* **2002**, *18*, 2013–2018.
- (27) Schilli, C. M.; Zhang, M. F.; Rizzardo, E.; Thang, S. H.; Chong, Y. K.; Edwards, K.; Karlsson, G.; Muller, A. H. E. *Macromolecules* **2004**, *37*, 7861–7866.
- (28) Arleth, L.; Xia, X. H.; Hjelm, R. P.; Wu, J. Z.; Hu, Z. B. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 849–860.
- (29) Chen, S. F.; Jiang, L.; Dan, Y. *J. Appl. Polym. Sci.* **2011**, *121*, 3322–3331.
- (30) Chen, G. H.; Hoffman, A. S. *Nature* **1995**, *373*, 49–52.
- (31) Khan, A. J. *Colloid Interface Sci.* **2007**, *313*, 697–704.
- (32) Yin, X. C.; Hoffman, A. S.; Stayton, P. S. *Biomacromolecules* **2006**, *7*, 1381–1385.
- (33) Romeo, G.; Fernandez-Nieves, A.; Wyss, H. M.; Acierno, D.; Weitz, D. A. *Adv. Mater.* **2010**, *22*, 3441–3445.
- (34) Liétor-Santos, J. J.; Sierra-Martín, B.; Fernández-Nieves, A. *Phys. Rev. E* **2011**, *84*, 060402.
- (35) Kolarik, J. *J. Macromol. Sci., Part B: Phys.* **1978**, *B15*, 371–380.
- (36) Xu, H. Y.; Guan, L. *J. Macromol. Sci., Part B: Phys.* **2011**, *50*, 956–966.
- (37) Castellano, C.; Pozzi, D.; Caracciolo, G.; Cantelli, R. *Appl. Phys. Lett.* **2003**, *83*, 2701–2703.
- (38) Maggi, C.; Jakobsen, B.; Christensen, T.; Olsen, N. B.; Dyre, J. C. *J. Phys. Chem. B* **2008**, *112*, 16320–16325.
- (39) Jakobsen, B.; Niss, K.; Olsen, N. B. *J. Chem. Phys.* **2005**, *123*, 234511.
- (40) Casalini, R.; Roland, C. M. *J. Chem. Phys.* **2009**, *131*, 114501.
- (41) Nowick, A. S.; Berry, B. S. *Anelastic Relaxation in Crystalline Solids*; Academic Press: New York, 1972; Chapters 1–6.
- (42) Angelini, R.; Giura, P.; Fioretto, D.; Monaco, G.; Ruocco, G.; Sette, F. *Phys. Rev. B* **2004**, *70*, 224302.
- (43) Shibayama, M.; Yoshizawa, H.; Kurokawa, H.; Fujiwara, H.; Nomura, S. *Polymer* **1988**, *29*, 2066–2071.
- (44) Meersman, F.; Geukens, B.; Wubbenhorst, M.; Leys, J.; Napolitano, S.; Filinchuk, Y.; Van Assche, G.; Van Mele, B.; Nies, E. *J. Phys. Chem. B* **2010**, *114*, 13944–13949.