

Division of Multidisciplinary Chemistry - Molecular Rheology -

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Scope of Research

The molecular origin of various rheological properties of materials is studied. Depending on time and temperature, homogeneous polymeric materials exhibit typical features of glass, rubber, and viscous fluid while heterogeneous polymeric systems exhibit plasticity in addition to these features. For a basic understanding of the features, the molecular motion and structures of various scales are studied for polymeric systems in deformed state. Measurements are performed of rheological properties with various rheometers, of isochronal molecular orientation with flow birefringence, and of auto-correlation of the orientation with dynamic dielectric spectroscopy.

Research Activities (Year 2005)

Presentations

Detailed Investigation of Entanglement Dynamics with Dielectric and Viscoelastic Methods, Watanabe H, 2nd Annual European Rheology Conference, Grenoble - France, 21 - 23 April.

Rheology of Block Copolymer Micellar Dispersion, Watanabe H, POLYCHAR-13, Singapore (Singapore). 3 - 8 July.

Tube Dilation in Entangled melts: Hierarchical Relaxation and Self-Consistent Coarse-Graining, Watanabe H, 5th International Discussion Meeting on relaxations in Complex Systems: New results, Directions and Opportunities, Lille, France, 7 - 13 July.

Tube Dilation in Entangled melts: A Route of Molecular Description of Viscoelastic Relaxation, Watanabe H, Korea-Australia Rheology Meeting, Cairns (Australia), 17 - 20 July.

Dynamic Birefringence of Cyclic Olefin Copolymers, Inoue T, 4th Pacific Rim Conference on Rheology, Shanghai, China, 8 - 11 August.

Grants

Watanabe H, Grant-in-Aid for Scientific Research (B), Relationship between Loop Content and Rheological Behavior of Multi-block Copolymer System, 1 April 2005 - 31 March 2007.

Inoue T, Grant-in-Aid for Scientific Research (C), Rheology of Surfactant Solution: Nonlinear Elongation and Shear-induced Structure of Thread-like Micelles, 1 April 2005 - 31 March 2007.

Matsumiya Y, Grant-in-Aid for Young Scientists (B), Rheo-dielectric Study on Non-equilibrium Dynamics of Polyether/lithium Salt Mixture Systems, 1 April 2005 - 31 March 2007.

Dynamics of Polybutadienyl Lithium Chains Aggregated in Benzene

In nonpolar solvents, living monoanionic polymer chains having Li as the counter cation aggregate through the association of Li.¹ Experiments have revealed that dimeric and/or tetrameric star-like aggregates are formed as the main component.^{1,2} However, dynamics of the aggregates was not elucidated. For this problem, ⁷Li-NMR and viscosity measurements were conducted for polybutadienyl lithium (PBLi) chains in deuterated benzene (d-Bz) to examine the lifetime τ_{life} and dissociation kinetics of the associated Li domains.³ The results are summarized below.

Figure 1 compares the viscosity η_{PB} in the living anionic and deactivated states (unfilled and filled symbols) for the PB/d-Bz solutions with the molecular weight M and the concentration C as indicated. At all temperatures T examined, η_{PB} is larger in the living state, demonstrating the aggregate formation of the living PB chains. A separate scattering experiment showed that tetrameric star-like aggregates were formed as the main component.³

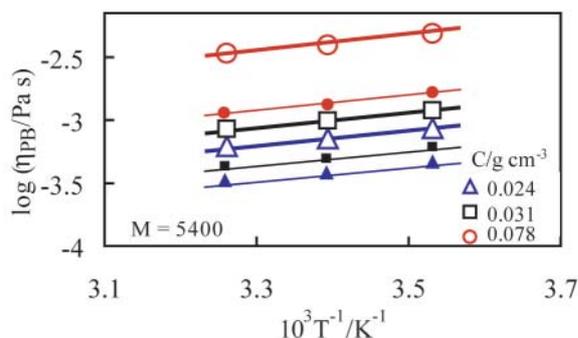


Figure 1. Viscosities of the living and deactivated PB chains (unfilled and filled symbols) with M and C as indicated.

Figure 2 shows the ⁷Li-NMR spectra of the PBLi/d-Bz solutions with M and C as indicated. The triple peak seen at low T suggests that Li cations are in several different aggregation states and the exchange of these Li species at low T is slow compared to the NMR time scale. With increasing T , this triple peak merges into single peak and thus the exchange becomes faster than the NMR time scale. Analysis of the spectra gave an average lifetime τ_{life} of the Li domain determined by this exchange.³ In the top panel of Figure 3, τ_{life} for various M and C are plotted against T^{-1} . The Arrhenius behavior is observed for respective M and C , but the magnitude of τ_{life} is strongly dependent on M and C . The origin of these dependencies is discussed below.

Since the activation energy of τ_{life} ($\approx 90 \text{ kJ mol}^{-1}$) is considerably lower than the bare Li-Li bond energy⁴ ($\approx 150 \text{ kJ mol}^{-1}$), the exchange of the Li species should have

occurred cooperatively through formation of a larger transient aggregate. This cooperative exchange (occurring at the rate of $1/\tau_{\text{life}}$) requires the PBLi tetrameric aggregates to collide each other against an osmotic barrier ΔG_{os} . A time τ_{dif} required for the diffusion over a distance between the aggregates was evaluated from the η_{PB} data (Figure 1), and ΔG_{os} was estimated from the osmotic data in literature.³ In the bottom panel of Figure 3, τ_{life} for various M and C are normalized by $\tau_{\text{dif}}Q_{\text{os}}$ ($Q_{\text{os}} = \exp(\Delta G_{\text{os}}/k_{\text{B}}T)$ with k_{B} being the Boltzmann constant) and plotted against T^{-1} . The normalized lifetime $\tau_{\text{life}}/\tau_{\text{dif}}Q_{\text{os}}$ is almost universally dependent on T irrespective of M and C . This result demonstrates that the dissociation kinetics of the aggregates is determined by not only the neat Li chemistry but also the polymeric character of the constituent chains reflected in the diffusion time and osmotic barrier.

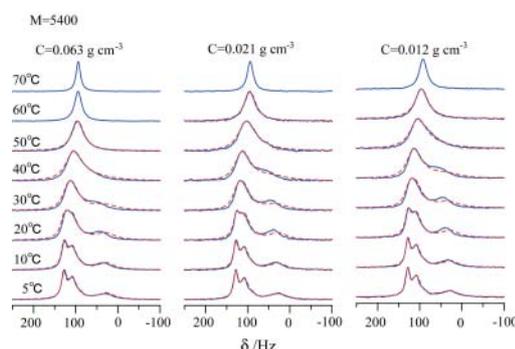


Figure 2. ⁷Li-NMR spectra obtained for living PB chains with M and C as indicated (solid curves). The dotted curves indicate the spectra reproduced from the analysis.

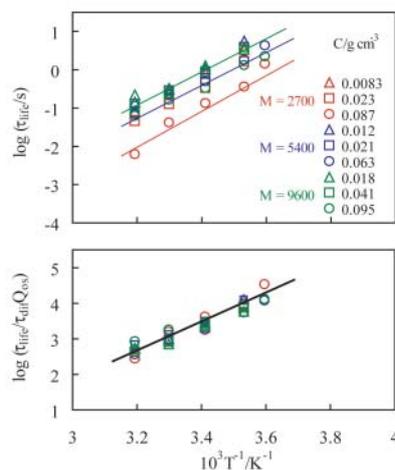


Figure 3. The average lifetime (Li-Li exchange time) τ_{life} for the living PB chains with M and C as indicated. Top and bottom panels indicate the plots of raw τ_{life} data and normalized $\tau_{\text{life}}/\tau_{\text{dif}}Q_{\text{os}}$, respectively.

[1] M. Morton, "Anionic Polymerization: Principles and Practice", Academic Press, New York, 1983.

[2] A. Z. Niu et al., *J. Chem. Phys.*, **122**, 134906 (2005).

[3] Y. Oishi et al., *Polymer J.*, in press.

[4] A. Frischknecht and S. T. Milner, *J. Chem. Phys.*, **114**, 1032 (2001).