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<td>岡田洋和; 田島義晴; 甲斐浩一; 井上京子; 朝地健人</td>
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<td>議論</td>
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Fundamental Material Properties - Molecular Dynamic Characteristics -

Prof HIRII, Fumitaka (D Eng)
Assoc Prof TSUNASHIMA, Yoshisuke (D Eng)
Instr KAJI, Hironori (D Eng)
Instr HIRAI, Asako (D Eng)

Techn OHMINE, Kyoko
PD (JSPS) MASUDA, Kenji (D Eng)

Students
ISHIDA, Hiroyuki (D6) MURAKAMI, Miwa (D2)
KUSAKA, Yasunari (D1) YAMADA, Shusaku (D1)
FUKE, Kazunori (M2) NAKAMURA, Hisako (M2)
INUI, Nobuhiko (M1) ONODERA, Gen (M1)
NISHIMURA, Takuya (M1) TSUJITANI, Kouji (B4)

Scope of Research

The research activities in this subdivision cover structural studies and molecular motion analyses of polymers and related low molecular weight compounds in the crystalline, glassy, liquid crystalline, solution, and frozen solution states by high-resolution solid-state NMR, dynamic light scattering, electron microscopy, X-ray diffractometry, and so on, in order to obtain basic theories for the development of high-performance polymer materials. The processes of biosynthesis, crystallization, and higher-ordered structure formation are also studied for bacterial cellulose.

Research Activities (Year 2001)

Presentations

Dynamic Clustering of Cellulose Triacetate in Solution as Measured by Dynamic Light Scattering (Prague, Czech), Tsunashima Y, IUPAC Czech Chemical Society, 11 July.

Dissipative Structures and Non-Ergodic Scattering in Solution of Cellulose Acetates in Couette Flow (New York, USA), Tsunashima Y, SUNY Chemical Society, 14 December.
Dynamic Self-Assemblies of Cellulose Acetates in Polar Solvents

Abstract. Dynamics of cellulose diacetates (CDA), the degree of substitution $DS = 2.44$, $M_w = 1.70 \times 10^5$, $M_w/M_n = 1.23$ in polar solvents, dimethylacetamide (DMAc), was investigated at $2-60^\circ C$ through dynamic light scattering (DLS) in quiescent state. CDA formed a few types of structures in polar solvents; a single CDA chain and the dynamical self-assemblies due to concentration fluctuations, which were created temporarily and locally by a solvent-mediated hydrogen bonding between the inter-molecular C-6 position hydroxyl groups. In addition, CDA showed low-temperature solubility; CDA was expected to dissolve molecularly below $–20^\circ C$, but to take a phase separation above $65^\circ C$, and exhibited a chain reorganization in dynamic structures around a middle temperature $T^* = 34^\circ C$. Both the correlation length and the dynamical second virial coefficients of the dynamic structures gave a discontinuity, maximum, or minimum at $T^*$. These dynamic features could correspond to the critical fluctuations and the LCST behavior provided that $T^*$ were regarded as the critical temperature.

Discussion. CDA took three translational modes in DMAc, i.e., the single chain diffusion (Mode I) and two dynamical fluctuations (Modes II and III). The former gave the hydrodynamic radius $R_H$ and the latter the correlation lengths $\xi_{II}$ and $\xi_{III}$. The temperature dependence of these sizes in the temperature range of $2-62^\circ C$ shows a unique feature. In contrast to the monotonic increase of $R_H$ with decreasing temperature (Mode I), $\xi_{II}$ and $\xi_{III}$ seem to show a singularity around $T^* = 33.8^\circ C$ in the way that they rise sharply toward a maximum or an infinity from both sides of $T^*$. In addition, $\xi_{II}$ and $\xi_{III}$ disappear below $–12^\circ C$, and come to join into a small value above $65^\circ C$. These two features indicate that the molecular dispersion of the single chain can be achieved below $–12^\circ C$ and two phase separation occurs above $65^\circ C$. Thus, CDA is in the low temperature solubility system, i.e., stable at lower temperature. The extreme increase of $\xi_{II}$ and $\xi_{III}$ at $T^*$ means that Modes II and III would amplify their concentration fluctuations excessively and critically as $T$ approaches to $T^*$.

In accordance with the change in $\xi$, the dynamical second virial coefficients $k_{D,II}$ for the single chain changes its sign from positive (repulsive) to negative (attractive) at $T^*$, while $k_{D,III}$ and $k_{D,III}$ for the assemblies are always negative but take zero or discontinuity at $T^*$. The state that $k_{D,II} = k_{D,III} = 0$ would mean that the chains are unstable and that a variety of cluster formation would be amplified at $T^*$ because the intermolecular interactions are apparently cancelled out under a delicate balance between multi-order interactions acting on the chains. We could thus have an image that $T^*$ is a critical temperature in the LCST system. The peculiarity in $\xi_{II}$ and $\xi_{III}$ around $T^*$ could be recognized as the dynamic critical fluctuation. This image can be verified by double-logarithmically plotting $\xi$ and $R_H$ against $|T - T^*|$, as is the case for the usual critical phenomena. The critical exponent $\nu$ in the expression that $\xi \propto |T - T^*|^{\nu}$ was given as $0.15, 0.68$, and $1.5$ for $\xi_{II}, \xi_{III}$, and $R_H$ at $T > T^*$, respectively. The value $\nu = 0.68$ is close to the theoretical one, $0.625$. The self-assemblies discussed above are formed in a nest of structures as illustrated by Figure below, where the temporarily created excess-concentration-fluctuations c(x) at a given time spot are plotted against the local space $x$.

Grants

Horii F, Studies on effects of dynamics factors and hydrogen bonding on structure formation for main-chain thermotropic liquid crystalline polymers, Grant-in Aid for Scientific Research (B)(2), 1 April 2000 -31 March 2002.


Kaji H, Precise analyses of polymorphous structure and dynamics by advanced solid-state NMR, Grant-in Aid for Young Scientists (A), 1 April 2001 -31 March 2003.