# Dynamic light scattering study on a bimodal end-linked polydimethylsiloxane network structure

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*(Received 20 June 1991; revised 29 August 1991)*

The cooperative diffusion coefficient $D_{\mathrm{coop}}$ and the normalized variance $\mu_2\bar{\Gamma}^{-2}$ for bimodal end-linked polydimethylsiloxane (PDMS) networks were determined by means of dynamic light scattering (DLS) measurements. $D_{\mathrm{coop}}$ was proportional to polymer weight concentration at the equilibrium state of swelling $C_e$ to the power of 0.88, which was larger than the theoretical exponent, compared with the unimodal PDMS networks. Further, the value of $\mu_2\bar{\Gamma}^{-2}$ at the lowest $C_e$ was greater than that of the corresponding bimodal PDMS solutions in the semidilute regime, and the autocorrelation function of DLS could be reproduced by a double-exponential fitting. These facts suggested a spatially and compositionally heterogeneous structure of bimodal PDMS networks, especially in the case of the lowest $C_e$.

**(Keywords: dynamic light scattering; polydimethylsiloxane; bimodal network)**

## INTRODUCTION

Dynamic light scattering (DLS) is a powerful technique to investigate dynamic properties of polymer solutions and swollen gels[1]. In a previous paper, the relationship between network structure and swelling mechanism was discussed from DLS measurements of unimodal end-linked polydimethylsiloxane (PDMS) networks[2].

On the other hand, bimodal end-linked PDMS networks prepared by an end-linking of two kinds of long and short PDMS prepolymers with different (average) molecular weight exhibit some characteristic mechanical properties[3]. Mark *et al.* have proposed that the origin may be due not to a spatially and compositionally heterogeneous structure in bimodal networks but to a non-Gaussian effect arising from limited long chain extensibility at high deformation[3], which is in contrast to the prediction of the weakest-link theory based upon affine deformation[4]. In another study, it was remarked that such properties of bimodal PDMS networks could be accounted for by the high dissipation of elastic energy, which occurs owing to the low mobility of long chains through 'clusters' of short chains and non-affine rearrangement of junctions and attached short chains[5]. This explanation suggests a certain heterogeneous network structure.

As described above, bimodal network structure has not been necessarily revealed in connection with mechanical properties. In this paper, bimodal end-linked PDMS network structure will be discussed in detail using the DLS technique.

## EXPERIMENTAL

### *Sample preparation*

Bimodal PDMS networks used in this study were prepared in the bulk state by end-linking two kinds of nearly monodispersed PDMS prepolymers (Toshiba Silicon Co. Ltd), which were, respectively, α,ω-divinyl PDMS-A of short chain (number-average molecular weight $M_{\mathrm{n,A}} = 2.53 \times 10^3$) and PDMS-D of long chain ($M_{\mathrm{n,D}} = 4.14 \times 10^4$). The detailed procedures used are described elsewhere[6]. Benzene (Bz) was used as a swelling solvent. The characterization of the samples is summarized in *Table 1*. Here, $M_{\mathrm{n,calc}}$ is the number-average molecular weight of the mixture of prepolymers, and is given by:

$$M_{\mathrm{n,calc}} = \bar{x}_{\mathrm{A}} M_{\mathrm{n,A}} + \bar{x}_{\mathrm{D}} M_{\mathrm{n,D}} \tag{1}$$

where $\bar{x}_{\mathrm{A}}$ and $\bar{x}_{\mathrm{D}}$ are the molar fractions of PDMS-A and PDMS-D, respectively. Further, SAD-8 in *Table 1* represents Bz 'solutions' of the mixture of PDMS prepolymers. The composition was always the same as that of AD-8, even if the total polymer weight concentration was changed.

**Table 1** Preparation and characterization of bimodal end-linked PDMS networks

| Sample | Content of PDMS-A wt% | Content of PDMS-A mol% | $M_{\mathrm{n,calc}}$[a] (mol$^{-1}$) | $C_e$[b] (kg m$^{-3}$) |
|---|---|---|---|---|
| AD-2 | 80 | 98.3 | $3.71 \times 10^3$ | $3.02 \times 10^2$ |
| AD-4 | 60 | 95.7 | $5.08 \times 10^3$ | $2.46 \times 10^2$ |
| AD-6 | 40 | 90.8 | $7.64 \times 10^3$ | $1.67 \times 10^2$ |
| AD-8 | 20 | 78.9 | $1.39 \times 10^4$ | $7.33 \times 10^1$ |
| SAD-8[c] | 20 | 78.9 | $1.39 \times 10^4$ | - |

[a] Number-average molecular weight of the mixture of PDMS prepolymers calculated using equation (1)
[b] Polymer weight concentration of swollen networks at the equilibrium state of swelling, which was measured at 293.15 K in benzene
[c] Composition of SAD-8 was always the same as that of AD-8, even if the total polymer weight concentration was changed
PDMS-A: $M_n = 2.53 \times 10^3$; PDMS-D: $M_n = 4.14 \times 10^4$

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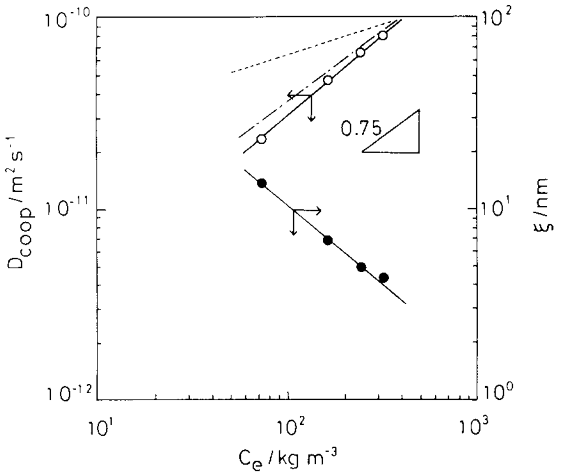

**Figure 1** Relationship between cooperative diffusion coefficient $D_{coop}$ (○) and polymer weight concentration at the equilibrium state of swelling $C_e$ for swollen bimodal end-linked PDMS networks, and the plot of the correlation length $\xi$ (●) *versus* $C_e$. ·—·, $D_{coop}$ of unimodal end-linked PDMS networks[2]. ···, Values of $D_{coop,calc}$ for bimodal networks calculated by equation (4). The numerical value, 0.75, shown in the figure is the exponent predicted from both the dynamic scaling law and the $C^*$ theorem

### *DLS measurement and analysis*

The DLS apparatus, conditions of measurement and the treatment of samples are described in detail elsewhere[2]. DLS was measured using homodyne spectroscopy[1] at 293.15 K. The optical system using the polarization microscope was designed and constructed so that the scattering angle $\theta$ was fixed only at 90°. The photon correlator was LPA-3000 (Ootsuka Electronics Co. Ltd).

An average decay constant $\bar{\Gamma}$ of the normalized first-order intensity autocorrelation function of photoelectric field $|g^{(1)}(\tau)|$, where $\tau$ is the correlation time, and the normalized variance $\mu_2\bar{\Gamma}^{-2}$ were determined by the second-order cumulant method[7]. One can obtain the cooperative diffusion coefficient $D_{coop}$ from the value of $\bar{\Gamma}$: $\bar{\Gamma} = q^2 D_{coop}$, where $q$ indicates the scattering vector[1]. In addition, so-called double-exponential (DE) fitting, as expressed by the following equation, was applied to $|g^{(1)}(\tau)|$[8]:

$$|g^{(1)}(\tau)| = A\exp(-\Gamma_f\tau) + (1-A)\exp(-\Gamma_s\tau) \qquad (2)$$

where $\Gamma_f$, $\Gamma_s$ and $A$ are, respectively, the decay constants of the fast and the slow modes and the relative amplitude (or scattering intensity) of the fast mode. The correlation length $\xi$ was expressed by[1,9]:

$$\xi = k_B T/6\pi\eta_0 D_{coop} \qquad (3)$$

where $k_B$ and $T$ are Boltzmann's constant and absolute temperature, respectively. The dependence of the viscosity of a swelling solvent $\eta_0$ in a swollen network on polymer weight concentration at the equilibrium state of swelling $C_e$ was assumed to be negligible[10], and the viscosity of the solvent was taken to be $\eta_0$.

All experimental results in the present study have satisfied the following requirement[1]: $q\xi < 1$. The systematic errors on calculation of the cumulant analysis and of the DE fitting were ~5–10%.

## RESULTS AND DISCUSSION

*Figure 1* indicates the relationship between $D_{coop}$, $\xi$ and $C_e$ for bimodal PDMS networks swollen in Bz. $D_{coop}$ increased with $C_e$, since the restoring force (due to the osmotic pressure in swollen networks) is stronger at high $C_e$ (ref. 9) and the values of $\xi$ calculated by equation (3) decreased with $C_e$, corresponding to the increase in $D_{coop}$. $D_{coop}$ was proportional to $C_e$ to the power of 0.88, which was larger than the exponent predicted from both the dynamic scaling law and the $C^*$ theorem[9], i.e. 0.75, and was also in contrast to 0.74 for unimodal PDMS networks (·—· line in *Figure 1*)[2]. $D_{coop}$ of bimodal networks became smaller than that of unimodal ones as $C_e$ decreased accompanying an increase in weight fraction of long chains of PDMS-D.

It should be borne in mind that the linearity of the plots of $\bar{\Gamma}$ *versus* $q^2$ has not been investigated because $\theta$ cannot be varied with the apparatus used[2]. However, the experimental condition of $\theta = 90°$ is frequently preferred in the case of DLS measurements of swollen gels because the strength of scattering light is generally weak, dust in swollen gels cannot be perfectly removed and stray light on the wall of the cell and/or a mode of intramolecular motion along long network chains at (much) lower $C_e$ can be effectively negligible[2].

At present only the following relation for the estimation of $D_{coop}$ of bimodal end-linked networks has been proposed[11]:

$$D^{-1}_{coop,calc} = \frac{\sum \nu_i D^{-1}_{coop,i}}{\sum \nu_i} \qquad (4)$$

where $\nu_i$ is the number of elastic network chains of type $i$ in the bimodal network, and $D_{coop,i}$ is the value of $D_{coop}$ for a unimodal end-linked network composed of the same type $i$ prepolymers. Equation (4) was based on the assumption that the overall elastic modulus $E$ and the friction constant $\Phi$ of bimodal networks, whose ratio equals $D_{coop}$[1,12], are independently given by the sum of $E_i$ or $\Phi_i$ of the $i$th unimodal network, respectively. The dotted line in *Figure 1* indicates the values of $D_{coop,calc}$, when $D_{coop,A}$ and $D_{coop,D}$ are, respectively, taken as $9.96 \times 10^{-11}$ and $2.09 \times 10^{-11}$ $m^2 s^{-1}$ in equation (4)[2]. Unfortunately, the experimental results in *Figure 1* cannot be explained by employing equation (4). Thus far the validity of equation (4) has not been checked satisfactorily*, and the above-mentioned assumption, that is, the simple additivity of the number of elastic network chains with different average molecular weight between crosslink sites against overall elastic modulus is thought to be in conflict with the basic concept in the statistical theory of ideal rubber-like elasticity[13].

*Figure 2* depicts the variations of $\mu_2\bar{\Gamma}^{-2}$ with $C_e$. The values of $\mu_2\bar{\Gamma}^{-2}$ for unimodal PDMS networks were nearly constant[2], whereas the same quantities were clearly dependent on $C_e$ in bimodal PDMS networks. In addition, it is noteworthy that the absolute value of $\mu_2\bar{\Gamma}^{-2}$ for AD-8 was larger than that of SAD-8 in the semidilute range, which is drawn as the horizontal line in *Figure 2*, although it is well-known that $\mu_2\bar{\Gamma}^{-2}$ approximately becomes zero for a single exponential decay of $|g^{(1)}(\tau)|$ after gelation[1,9,12].

The experimental results in *Figures 1* and *2* suggest a certain heterogeneous structure in bimodal networks, and so $|g^{(1)}(\tau)|$ was analysed again by DE fitting. Here, the so-called heterodyne effect was assumed to be

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* A sample in reference 11 was only one bimodal end-linked polystyrene gel with high $C_e$, and $D_{coop,calc}$ was in good agreement with the experimental result at $C_e$

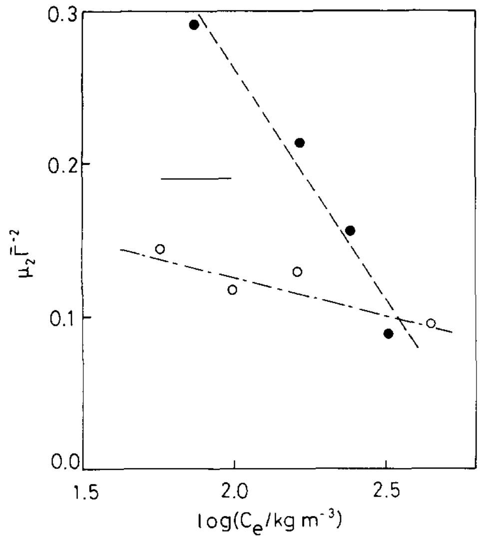

**Figure 2** Dependence of normalized variance $\mu_2\Gamma^{-2}$ on $C_e$ for unimodal[2] (○) and bimodal (●) PDMS networks. The horizontal line displays the value of $\mu_2\Gamma^{-2}$ of SAD-8 in the semidilute regime

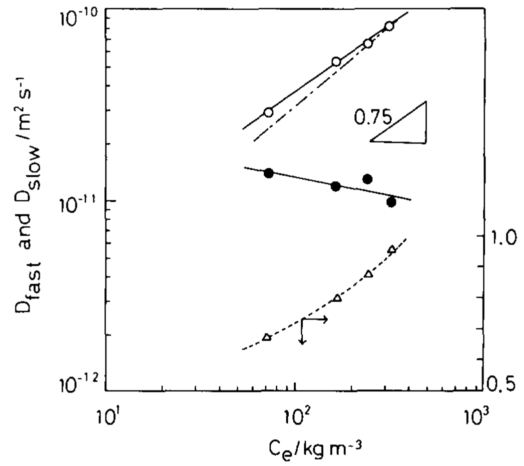

**Figure 3** Variations of two kinds of diffusion coefficients $D_{fast}$ (○) and $D_{slow}$ (●) of the fast and slow modes, respectively, and of relative amplitude (or scattering intensity) of the fast mode $A$ (△) in equation (2) with $C_e$. ·—·, Values of $D_{coop}$ determined by the cumulant method, which are identical to those in *Figure 1*. The physical meaning of the numerical value is also the same as in *Figure 1*

negligible[14]. This seems to be experimentally reasonable because all the samples were optically clear and $|g^{(1)}(\tau)|$ measured at any position in one sample gave the same decay curves. It follows that there hardly exists any voids and/or dust in the samples used.

*Figure 3* shows the dependence of the diffusion coefficients $D_{fast}$ and $D_{slow}$ of the fast and slow modes and of A in equation (2) on $C_e$. $D_{fast}$ was proportional to $C_e$ to the power of 0.73, and the exponent is approximately compatible with the theoretical prediction[1,9], while $D_{slow}$ decreased slightly with $C_e$. (The straight line was drawn with the least-squares method.) However, systematic errors in the calculation of $D_{slow}$ should be anticipated to be larger at high $C_e$, since the value of $A$ was almost equal to unity.

Now, one must assign these two decay modes with caution. In the present study, the fast mode was assigned to the cooperative diffusion mode of network chains, which is substantiated by the dependence of $D_{fast}$ on $C_e$. On the other hand, the slow mode represents a self-diffusion mode of a certain size of cluster as a whole in bimodal networks. This assignment was proposed by reference to the theory of Pusey *et al.*[15], *in situ* investigation of gelation of polystyrene (PS) with DLS[16] and DLS studies on transient networks of PS solutions in the semidilute regime[14,17,18]. In these cases, the origins of the slow mode were due to clustering of branched PS chains before and after gelation in the former case, and due to the centre-of-mass translational motions of entangled chains in a transient network in the latter case. The above 'cluster (region)' in bimodal PDMS networks is considered to correspond to small mesh domains, which are formed by many short chains.

Consequently, bimodal end-linked PDMS networks prepared in the bulk state, especially AD-8, may not be a homogeneous structure as shown in *Figure 4a*, where long and short chains are randomly end-linked to each other, but probably a spatially and compositionally non-random heterogeneous structure (*Figure 4b*), which is made up of small mesh domains and large ones. It can be assumed that the formation of such a network structure is due to higher probability of end-linking of short chains than that of long chains, which is also closely related to the compositions. Stein *et al.* have reported a similar network structure through the static light scattering measurements on the same system[19] and a segregation of crosslink sites in bimodal networks of polytetrahydrofuran[20].

Small mesh domains may contribute to a self-reinforcement and/or toughness as a filler effect in stress–strain behaviours of bimodal PDMS networks[5].

However, it is difficult to express quantitatively the heterogeneity of such a bimodal network structure, e.g. an average size and a distribution of small mesh domains, and an average distance between domains. For example, even if one calculates $\xi$ from $D_{slow}$ by employing equation

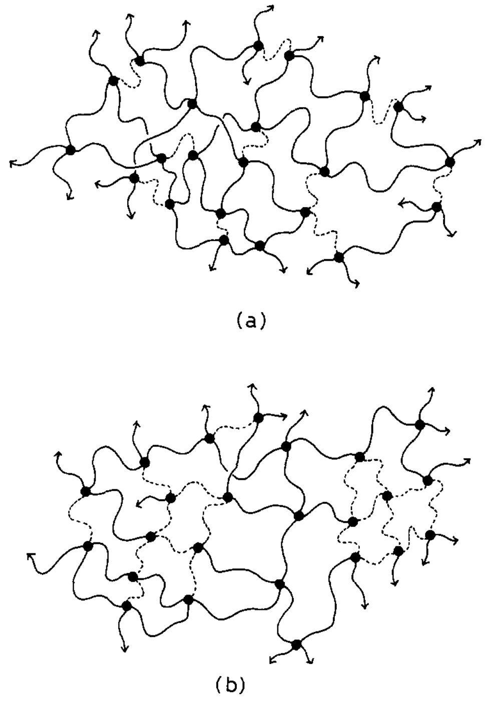

**Figure 4** Proposed scheme of bimodal network structure: (a) random homogeneous end-linking; (b) spatially and compositionally non-random heterogeneous end-linking. The solid and dotted lines represent long and short chains of PDMS prepolymers, respectively

(3), this quantity cannot be regarded precisely as an average size of domains, since the slow mode is neither a cooperative diffusion mode nor a translation self-diffusion mode of free particles in this case[14,17,18].

## ACKNOWLEDGEMENTS

The author gratefully acknowledges the help received from Research Associate Dr K. Tsukamoto (Department of Mineralogy, Petrology and Economic Geology, Faculty of Science, Tohoku University) with the DLS measurements. The DLS equipment was made in his laboratory. Further, the author wishes to thank Associate Professor Dr K. Ono (Institute for Chemical Reaction Science, Tohoku University) for many useful suggestions.

## REFERENCES

1 Pecora, R. 'Dynamic Light Scattering', Plenum Press, New York, 1985
2 Oikawa, H. and Murakami, K. *Macromolecules* 1991, **24**, 1117
3 Mark, J. E. and Erman, B. 'Rubberlike Elasticity. A Molecular Primer', John Wiley & Sons, New York, 1988
4 Bueche, F. 'Physical Properties of Polymers', Wiley-Interscience, New York, 1962
5 Smith, T. L., Haidar, B. and Hedrick, J. L. *Rubber Chem. Technol.* 1990, **63**, 256
6 Oikawa, H. and Murakami, K. *Polymer* 1986, **27**, 1563
7 Koppel, D. E. *J. Chem. Phys.* 1972, **57**, 4814
8 Phillies, G. D. J. *J. Appl. Polym., Appl. Polym. Symp.* 1989, **43**, 275
9 De Gennes, P.-G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, 1979
10 Hecht, A. M. and Geissler, E. *J. Phys.* (*Les Ulis, Fr.*) 1978, **39**, 631
11 Munch, J. P. and Candau, S. *J. Polym. Sci., Polym. Phys. Edn* 1977, **15**, 11
12 Tanaka, T., Hocker, L. and Benedek, G. B. *J. Chem. Phys.* 1973, **59**, 5151
13 Treloar, L. R. G. 'The Physics of Rubber Elasticity', Clarendon Press, Oxford, 1975
14 Brown, W. and Johnsen, R. M. *Macromolecules* 1985, **18**, 379
15 Pusey, P. N., Fijnaut, H. A. and Vrij, A. *J. Chem. Phys.* 1982, **71**, 4270
16 Candau, S., Ankrim, M., Munch, J. P. and Hild, G. *Br. Polym. J.* 1985, **17**, 210
17 Brown, W. *Macromolecules* 1986, **19**, 1083
18 Brown, W. *Macromolecules* 1985, **18**, 1713
19 Soni, V. K. and Stein, R. S. *Macromolecules* 1990, **23**, 5257
20 Wu, W.-I., Coyne, L. D., Jong, L., Hanyu, A. and Stein, R. S. *Macromolecules* 1990, **23**, 351