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Molecular Probing of Polymeric Microstructure and Nonrandom Partitioning of Solvents Absorbed in Polymers by Inverse Gas Chromatography

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ABSTRACT: The microscopic structure of amorphous polymers was studied by using different molecular probes in finite dilution inverse gas chromatography (FDIGC) experiments. This molecular probe technique allows one to study nonrandom partitioning of solvent molecules and spatial correlation of polymer chain segments in a bulk. A novel approach was developed to determine cluster integrals as defined in the Kirkwood−Buff theory of mixtures. Solvent self-cluster integrals, a combination of cluster integrals expressing preferential solvation, and the values of the mean cluster size were determined for different polymer systems as a function of the volume fraction of the probe in the bulk of the polymers. Polymers with different polarities [a substituted poly(thionylphosphazene), a saturated polyester poly(diethylene glycol−succinic acid), and an essentially apolar poly(dimethylsiloxane)] were used as model materials. The microstructure and the solvent−polymer interaction are discussed in detail for each system. The results obtained allowed us to gain novel insight into the polymeric microstructure and short-range order, thus giving credibility to our approach to study microstructure by cluster integrals from inverse gas chromatography (IGC) data.

Introduction

The understanding of microscopic structures and short-range molecular order is important in designing and controlling the properties of specialty polymers for high-performance applications.[1] For example, small molecule clustering has an impact on the transport process in, e.g., separation techniques employing polymers and controlled release applications of polymeric materials.[2] In addition, solvent clustering behavior plays an important role in controlling the structure of porous materials obtained by polymerization,[3] the network structure in cross-linked materials,[4] etc.

Theories based on random mixing of polymer−solvent molecules have been developed to describe the sorption of solvents into polymeric materials.[5,6] However, difficulties are encountered when these theories are used to fit the sorption isotherms of poor solvents.[7] The nonmean field approaches, which give a fair description of the sorption, are hampered because of the complexity of the correlations from different potential forces and the covalent connectivity of units in a macromolecular chain.[1a,8]

Due to the great variety of possible microstructures of polymeric materials, characterization techniques that deliver molecular level information have played a crucial role in polymer science.[9] Information regarding the average spatial distribution of solvent molecules and of polymer segments can be obtained from molecular probe techniques by determining the concentration dependence of the probe chemical potential, or from scattering experiments by obtaining the scattering structure factor. Examples that describe nonrandom average spatial distribution in polymer solutions and blends by Kirkwoo−Buff−Zimm (KBZ) cluster integrals have been discussed in the literature.[10,11] In this paper we show how the technique of inverse gas chromatography (for reviews see, e.g., ref 12) can be applied to obtain KBZ cluster integrals, which have a very intuitive appeal for explaining molecular nonrandom partitioning and preferential solvation.

The concept of the cluster integrals was successfully used in investigating the structures and properties of polymeric materials. For example, various vapor phase measurements[13] were used to investigate the structures and molecular diffusion in ethylene polymers, styrene polymers, siloxane polymers,[7,14] natural and synthetic rubbers,[6a,14a,b,15] blends,[16] and hydrophilic polymeric materials[17] as well as polyelectrolyte complexes[18] in terms of cluster integrals. Other colligative experiments, such as vapor osmometry and sedimentation equilibrium,[19,20] have been useful for examining local distributions in solvent−polymer mixtures. Neutron scattering experimental data were used to discuss the structure of the compatible blend poly(vinyl methyl ether) and deuterated polystyrene[11] with cluster integrals.

FDIGC works at a low concentration regime of the solvent probes.[21] In such an experiment, the self-interaction of the probe is lessened in the polymer. Therefore, the mixing behavior of a probe with a polymer essentially depends on the original microstructure in the polymer. This makes FDIGC better than many other techniques for investigating the microstructures of polymeric materials.

Theoretical Background

Cluster Integrals. The spatial distribution of molecules in a polymer matrix can be described by the fluctuation in the molecular density and composition. One way of describing local composition deviations from the mean values is given by KBZ cluster integrals.[6b,22] These integrals are related to the molecular pair correlation function $g_{ij}(\mathbf{R})$. The $\mathbf{R}$ denotes vectors defining the relative position of the mass centers of the molecules

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in the phase space. The definition of the Kirkwood−Buff molecular cluster integrals, G_{ij}, is thus

$$G_{ij} = \int_V [g_{ij}(\mathbf{R}) - 1]\, \mathrm{d}\mathbf{R} \qquad (1)$$

The mean overall molecular number density of the species "i" is defined by $\rho_i = N_i/V$ where there are N_i molecules in the subsystem with volume V. The cluster integrals thus defined are doublet cluster integrals and form a matrix for a multicomponent system.[23] The value of the product $\rho_j G_{ij} = (=\delta N_{ij})$ describes the tendency of the molecules of type "j" to agglomerate around a molecule of type i, or alternatively, disperse from the vicinity of a typical molecule "i". This leads to local densities that are greater or less than the overall average. "Typical" in this instance refers to an average taken over the whole system. The intrinsic tendency of molecules of type "j" to gather around "i" type molecules can thus be described by the value of G_{ij}.[24] In order to normalize molecular size effects, it is convenient to introduce the ratio $G_{ij}/\bar{V}_j$ where $\bar{V}_j$ is the partial molar volume of particles "j". $G_{ij}/\bar{V}_j$ is equal to $\rho_j G_{ij}$ divided by the volume fraction, v_j, of the component j. The value of $G_{ij}/\bar{V}_j$ expresses the preferred spatial gathering of solvent or polymer mers around the specified "partner". At a given v_i, an increase of the value of $G_{ii}/\bar{V}_i$ corresponds to a greater tendency of the "i" molecules to form self-clusters. An increase of $G_{ij}/\bar{V}_j$ means an increasing affinity of "j" to gather around "i". Preferential solvation around "j" can also be given by $[G_{ij} - G_{lj}]/\bar{V}_j$. A positive value of $[G_{ij} - G_{lj}]/\bar{V}_j$ means favored preferential solvation of "i" around "j" compared to "l". The self-cluster integrals are directly related to the second virial coefficient by $G_{jj}^{\infty} = -2N_A B_{2,j}$ when the concentration becomes infinitesimal.[24] N_A is Avogadro's number, and ∞ denotes the infinite dilution with respect to j. The mean cluster size (MCS) of, e.g., the solvent, can be expressed by the product $\rho_1 G_{11}$ as follows

$$\mathrm{MCS} = \rho_1 G_{11} + 1 \qquad (2)$$

The value of solvent MCS corresponds to the excess number of solvent molecules around the centers of "typical" solvent molecules in the entire system.[20]

Of the methods for determining cluster integrals, scattering experiments and molecular probe measurements are particularly relevant to our discussion here. An excellent example for the thermodynamic approach is given by Ben-Naim[24] who used partial molar volumes, isothermal compressibility, and partial vapor pressures to obtain $G_{ij}/\bar{V}_j$ values in water−ethanol systems. Theory, model calculations, and experimental results regarding KBZ cluster integrals applied to polymers were reviewed by Horta in a series of two publications[11] based on the inverse Kirkwood−Buff theory.[10] The average number of particles in a cluster and the average cluster size for some polymer−solvent systems was discussed by Starkweather.[20] Scattering experiments measure the collective wave contribution of the Fourier transform of the fluctuation in a system, $\int_V \langle \Delta N_i \Delta N_j \rangle e^{iqR}\, \mathrm{d}\mathbf{R}\ (=[\bar{N}_i \bar{N}_j/V][G_{ij}(\mathbf{q}) + \delta_{ij}(\mathbf{q})/\rho_i])$, $\delta(\mathbf{q})$ is the Dirac δ-function.[25−27] For a binary solution, the scattering structure factor, as defined in the following, is the direct empirical quantity from the experiments.

The approach we adopted to obtain G_{ij} values from IGC includes the use of the mer−mer scattering structure factor $S^*(\mathbf{q})$ at $\mathbf{q} = 0$, where the $\mathbf{q}$ is the scattering vector.[10,11,26a] We follow here the work of Horta,[11] who has shown that the following expressions hold for the normalized molecular cluster integrals in binary mixtures

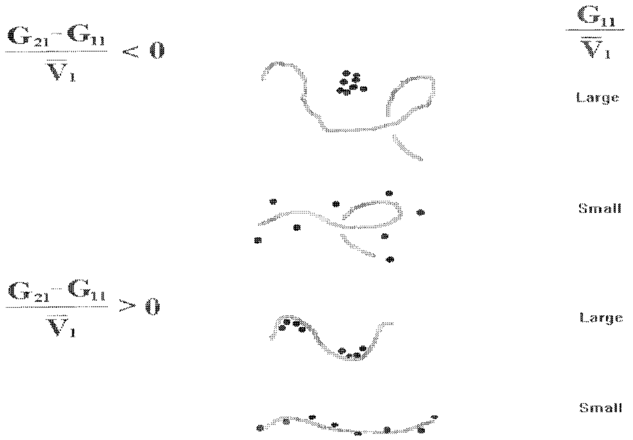

Figure 1. Pictorial view of the microstructure in a polymer bulk as classified with cluster integrals.

$$\frac{G_{11}}{\bar{V}_1} = \frac{1}{v_1}\left[\frac{S^*(0)}{v_1} - 1\right] \qquad (3)$$

$$\frac{G_{21} - G_{11}}{\bar{V}_1} = -\frac{1}{v_1}\left[\frac{S^*(0)}{v_1} - 1\right] - \frac{S^*(0)}{v_1 v_2} \qquad (4)$$

$S^*(0)$ is defined by[28]

$$S^*(0) = RTv_1 v_2 \left[\frac{\partial \mu_1}{\partial \ln v_1}\right]^{-1} = v_1 v_2 \left[1 - v_1 \frac{\partial \gamma_1}{\partial a_1}\right] \qquad (5)$$

This represents the structure factor for the correlation of the mers comprising the overall systems of the solvent and the polymer molecules, e.g., $S^*(0) = \langle (\Delta v)^2 \rangle$, when higher orders of fluctuation are neglected. With $S^*(0)$ these equations relate the mer−mer correlation with the molecular correlation, which is measurable from molecular probe experiments. γ_1 is the volume fraction based activity coefficient (i.e., $\gamma_1 = a_1/v_1$, where a_1 is the activity of the probe). These equations of molecular correlation are valid for both probe molecules and macromolecules if the relative size of the different molecules does not change with the composition. The compressibility term $RT\kappa_T$ has been neglected in order to reduce these equations, since its value, as estimated by Lunberg and Horta[10,11,15b] is usually very small compared to the concentration fluctuation terms. For an ideal solution, $\partial\gamma_1/\partial a_1 = 0$, $S^*(0) = v_1 v_2$, $G_{11}/\bar{V}_1 = -1$, and $[G_{21} - G_{11}]/\bar{V}_1 = 0$.

Pictorial View of Microstructure with Cluster Integrals. Cluster integrals are useful for forming mental pictures of the microstructures in polymeric mixtures. Specifically, convenient association, albeit tentative, can be made with the self-cluster integral and the preferential solvation to classify the possible structures into four groups (see Figure 1). Physically, there are many factors affecting the microstructure, including enthalpic and entropic factors such as the exchange potential of interactions, vacant sites, and the connectivity between the units in a macromolecule due to the chemical bonding. A negative value of the preferential solvation indicates that there is a mutual repulsion between solvent molecules and polymer molecules. For $[G_{21} - G_{11}]/\bar{V}_1 > 0$, the solvent has an affinity to the units in the polymer chains and the solvent molecules tend to stick to the chains. The solvent usually swells the chains locally or globally. A large value of the self-cluster integral of the probe in conjunction with the positive preferential solvation indicates that the solvent molecules are sticking onto a chain and most likely slide toward each other, forming clusters around the chain.

Understanding correlations from various sources of interactions in polymeric systems is important in the applications of polymeric materials.[29] Detailed models describing the microstructures of a chain and the bulk of materials of chain molecules have been rigorously formulated in recent years by employing either lattice spacing or continuous spacing.[1a,30] The most important feature of macromolecular systems is that a mer in a macromolecule can hold a second mer in the same molecule (with a number of chemical bonds) while the second mer interacts with mers in another macromolecule. This creates a unique correlation of macromolecules in the system.[8b] Nevertheless, a complete understanding of this phenomena is far too complicated for these theories to be used in practice.

An extensive mobility of molecules at a high temperature creates a large free volume in the system. The temperature has a strong effect on specific interactions and has hence a strong effect on the molecular correlation from specific interactions. For systems which have a specific interaction, the original polymer microstructure is usually more inhomogeneous because of the clustering due to the specific interaction between the units that make up the chains. Such systems have been proven to be better described by the high probability of the existence of vacant sites as “holes”.[6b,31] The connectivity of chemical bonding makes the units in a macromolecule more likely to come together so that the apparent effect is to produce a large value of the self-cluster integrals of the solvent.

Cluster Integrals from Finite Dilute Inverse Gas Chromatography.[21,32] In the elution-on-a-plateau (EP) method of FDIGC, a saturator containing a solvent probe is installed between the source of the inert carrier gas and the gas chromatographic column. When the temperature of the saturator is adjusted, the concentration of the solvent probe in the stream of the carrier gas can be controlled and kept constant. The basic idea of the EP method is to determine the amount of the solvent probe (carried by an inert gas) absorbed in the stationary phase of the column using the retention volume of the probe. This stationary phase includes the polymer being studied. Once the carrier gas (including the probe at a controlled vapor pressure) reaches an equilibrium flow through the stationary phase, the net retention volume, V_N, can be determined by injecting an additional small amount of the probe into the stream of the carrier gas. The value of V_N is then used to determine the concentration of the solvent in the stationary phase.

With the simplified Condor–Purnell treatment[21] of the finite concentration chromatographic procedure, the concentration of the solvent probe in the stationary polymeric phase, q, can be expressed

$$q = \frac{1}{w_p}\int_0^c \frac{jV_N(c')}{1 - \psi(c')}\,dc' \tag{6}$$

where q (in mol g^{-1}) (which corresponds to the amount of probe dissolved in 1 g of polymer, the polymer being the thermodynamic solvent) and c (in mol m^{-3}) are the concentrations of the solvent probe in the dissolved and vapor phases, respectively; j is a correcting factor that takes into account compressibility effects and nonideality of the gas phase; w_p is the weight of the polymer in the IGC column; and ψ is the corrected mole fraction of the solvent in the mobile phase. By using the value of q, the weight fraction of the solvent probe, w_1, in the stationary phase can be obtained

$$w_1 = \frac{qM_1}{1 + qM_1} \tag{7}$$

where M_1 is the molar mass of the solvent probe.

The thermodynamic activity, a_1, of the solvent in the stationary phase can be simply obtained by using the actual parameters of the IGC experiment.[33] The fundamental experimental information delivered by the FDIGC measurement includes the concentration of the solvent in the stationary phase and the activity of the solvent. In order to use the data of a_1 vs w_1 properly, we consider the interaction parameter, χ, to be a concentration dependent, effective quantity.

The experimental protocol for determining cluster integrals includes the following steps. First, the concentration dependence of the activity coefficient must be determined and fitted to the Flory–Huggins formula

$$\ln a_1 = \ln v_1 + \left(1 - \frac{1}{r}\right)v_2 + \chi {v_2}^2 \tag{8}$$

where r is the ratio of the molar volume of the macromolecules and the probe molecules. Secondly, eq 8 was substituted into eq 5 to obtain the values of $S^*(0)$ at different polymer volume fractions v_2. These $S^*(0)$ values are then used in eqs 3 and 4 to obtain the cluster integrals as a function of the volume fraction.

For each solvent–polymer system, a reference system can be defined to have the interaction parameter of this system at the infinite dilution of the solvent without the concentration dependence. Such a system can be fit to the Flory–Huggins model (FH model), and the inhomogeneity of it may be taken as a standard. The difference of the value of the tangent to the self-cluster integral curve between the real system and the reference system will be a reflection of the inhomogeneity increment of a real system from the standard. This contrast may give a quantitative comparison of the inhomogeneity (or correlation) of the microstructures of various systems. Therefore, we define a reduced self-cluster integral, G, by

$$G = \left[\frac{G_{11}}{\bar{V}_1}\right] - \left[\frac{G_{11}}{\bar{V}_1}\right]_{FH} \tag{9}$$

for the discussion of the inhomogeneity in the microstructure. The $[G_{11}/\bar{V}_1]_{FH}$ is the solvent self-cluster integral for the reference system.

Experimental Section

Apparatus and Materials. A setup to perform inverse gas chromatography measurements at finite concentrations of the solvent probes was built as described by Price and Guillet.[32b,34] The concentration of solvent probe was varied by a saturator condenser. The temperature of the condenser and of the columns was controlled by water thermostats with an accuracy of ±0.02 deg. The pressure in the saturator was measured

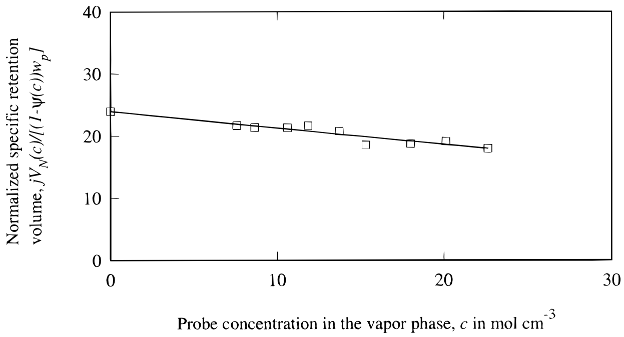

Figure 2. Reversed normalized retention diagram of CH_2Cl_2 in PCTTP at 50.0 °C.

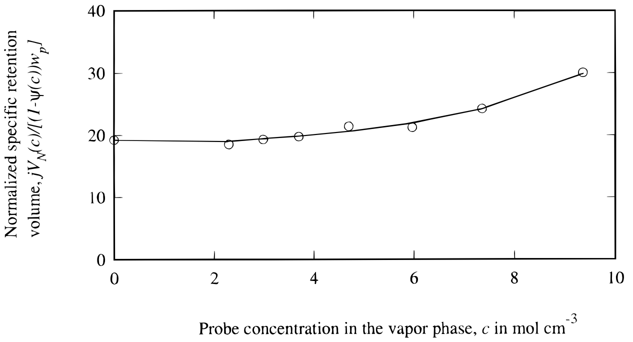

Figure 3. Reversed normalized retention diagram of *n*-hexane in PCTTP at 50.0 °C.

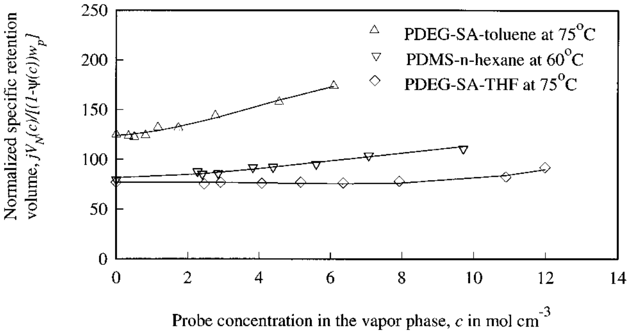

Figure 4. Reversed normalized retention diagram of the probes in PDEG−SA and PDMS.

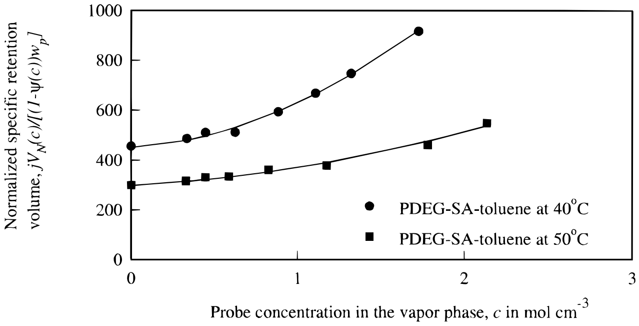

Figure 5. Reversed normalized retention diagram of toluene in PDEG−SA at 40.0 and 50.0 °C.

by a mercury manometer with an accuracy of ±0.2 Torr. Another mercury manometer was set up directly at the inlet of the sample-containing column to measure the inlet pressure P_{in}. The finite concentration experiments were always run at condition $\psi\Delta P/P_{in} < 1\%$. All temperatures were measured by ATM thermometers to within ±0.02 deg. The detector utilized was a twin-channel GOW MAC 40−001 thermoconductivity device. A sketch of the setup used in this study can be found in ref 32b (Figure 1). Other details are discussed elsewhere.[33]

Poly(dimethylsiloxane) (PDMS) was supplied by Polysciences Inc. with a number average molar mass of 3.6×10^4 g/mol. The polyester sample studied was a poly(diethylene glycol−succinic acid) (PDEG−SA) sample obtained by melt polycondensation, as described elsewhere.[35] The number average molar mass of this polymer was 1060 g/mol, and the polymer contained statistically equal amounts of −COOH and −OH chain-terminal groups. Poly(*S*-chloro-*P*-tetrakis(*m*-(trifluoromethyl)phenyl)thionylphosphazene) (PCTTP) was synthesized[36] with a polystyrene-effective average molar mass of 2.3×10^5 g/mol. The density of the materials was measured by using a pycnometer. The densities of the polymers as a function of temperature were described as follows

$$\text{PDMS} \qquad \rho_p = 0.9893 - 5.1000 \times 10^{-4}t - 1.000 \times 10^{-5}t^2 \tag{10}$$

$$\text{PDEG−SA} \qquad \rho_p = 1.2941 - 1.0132 \times 10^{-3}t \tag{11}$$

$$\text{PCTTP} \qquad \rho_p = 1.5566 - 1.0904 \times 10^{-3}t \tag{12}$$

in the range of temperature, *t*, between 30 and 80 °C. Coating the materials onto the solid support was carried out in the usual manner by employing good solvents for the polymers (*n*-hexane for PDMS, THF for PDEG−SA, and CH_2Cl_2 for PCTTP).[21] The loading percentages were 4.327% for PDMS, 4.074% for PDEG−SA, and 3.998% for PCTTP, respectively. The chromatographic support was Chromosorb G with 60/80 mesh size and a dimethyldichlorosilane-treated, acid-washed product supplied by Chromatographic Specialists Inc. The solvents were all analytical grade and were dried with molecular sieves before use. Ultrahigh purity helium was used as the inert carrier gas, which reduces the systematic error in the FDIGC calculation to a minimum. Preliminary results were published elsewhere.[37]

IGC Operation. Experiments were run on the blank column of Chromosorb G for all of the solvents to check the adsorption of the solvents under the same experimental conditions as for the sample columns. This step was necessary in order to correct for the adsorption of the solvents. Further details of FDIGC operation are given in ref 33.

Results and Discussion

Experiments were performed at several concentration plateau values to obtain plots of $jV_N/[(1 - \psi)w_p]$ vs concentration c (mol/m^3). The retention time was used to calculate the retention volume, which was used to obtain the value of $jV_N/[(1 - \psi)w_p]$. Plots of $jV_N/[(1 - \psi)w_p]$ vs c are shown in Figures 2−5 for various systems. Such a plot is, in fact, a normalized elution diagram at a finite concentration. Infinite dilution experiments were also performed, and the data are shown for reference on the *y*-axis. The data were fitted by using a polynomial equation and were then integrated with respect to the concentration of the probe in the vapor phase to obtain the value of q in eq 6. In the calculation of the activity, a_1, the Antoine equation was used to obtain $P_1^0(T)$.[38] The volume fraction of solvent in the stationary phase was calculated under the assumption that the volume of the polymer−solvent system is additive

$$v_1 = \frac{w_1/\rho_s}{[w_1/\rho_s + (1 - w_1)/\rho_p]} \tag{13}$$

and $v_2 = 1 - v_1$. Here ρ_s and ρ_p stand for the density of the solvent and the polymer, respectively. In order to obtain values of the cluster integrals for polymers with different solvent probes, results of FDIGC experiments were evaluated, as described earlier.

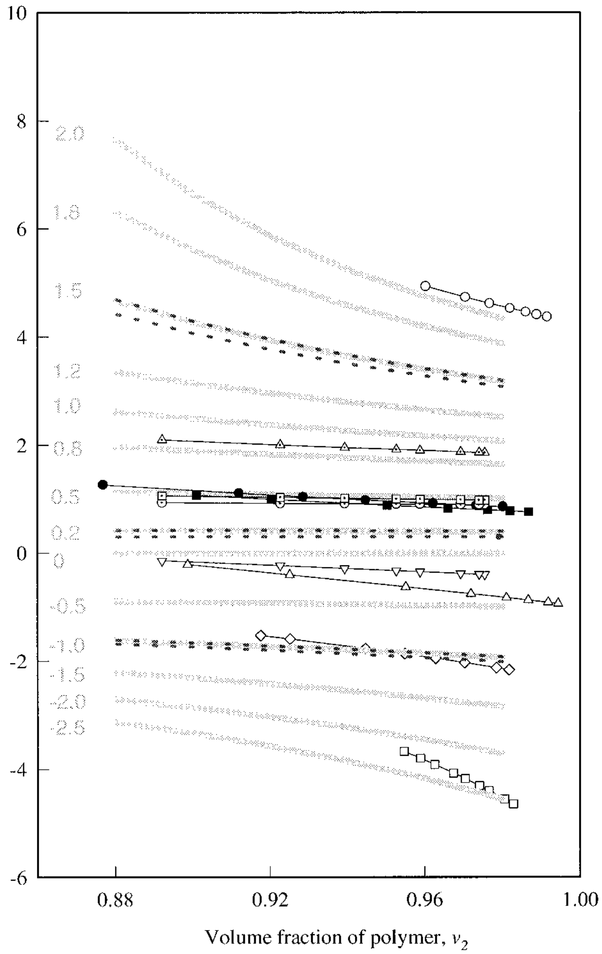

Figure 6. Comparison of self-cluster integrals for various polymer−solvent systems: (○) PCTTP−*n*-hexane at 50.0 °C; (◬) PDMS−benzene at 25.0 °C (interaction parameters taken from ref 32b); (●) PDEG−SA−toluene at 40.0 °C; (■) PDEG−SA−toluene at 50.0 °C; (⊡) PDMS−cyclohexane at 25 °C (interaction parameters taken from ref 32b); (⊙) PDMS−*n*-hexane at 25.0 °C (interaction parameters taken from ref 32b); (△) PDMS−*n*-hexane at 60.0 °C; (▽) PDEG−SA−toluene at 75.0 °C; (□) PCTTP−CH$_2$Cl$_2$ at 50.0 °C; (◇) PDEG−SA−THF at 75.0 °C.

The systematic error has been assessed by Price and Guillet using a vapor pressure experiment.[32b] The error in retention volume was estimated to be less than 2.5%. This is the major source of the statistical error. The other uncertainties concomitant with this 2.5% error in retention volume: solubility q < 2.9%; volume fraction v_1 < 3.0%; activity coefficient γ_1 < 3.6%; cluster integrals $[(G_{11}/\bar{V}_1) + 2] < 4.8\%$.

The plots for the cluster integrals are shown in Figures 6−8 together with the results calculated from data obtained by Price and Guillet for the systems of PDMS with *n*-hexane, cyclohexane, and benzene at 25 °C. The polymers studied were, from less to more polar, PDMS, PDEG−SA, and PCTTP. The solvents used were *n*-hexane, cyclohexane, benzene, toluene, and THF.

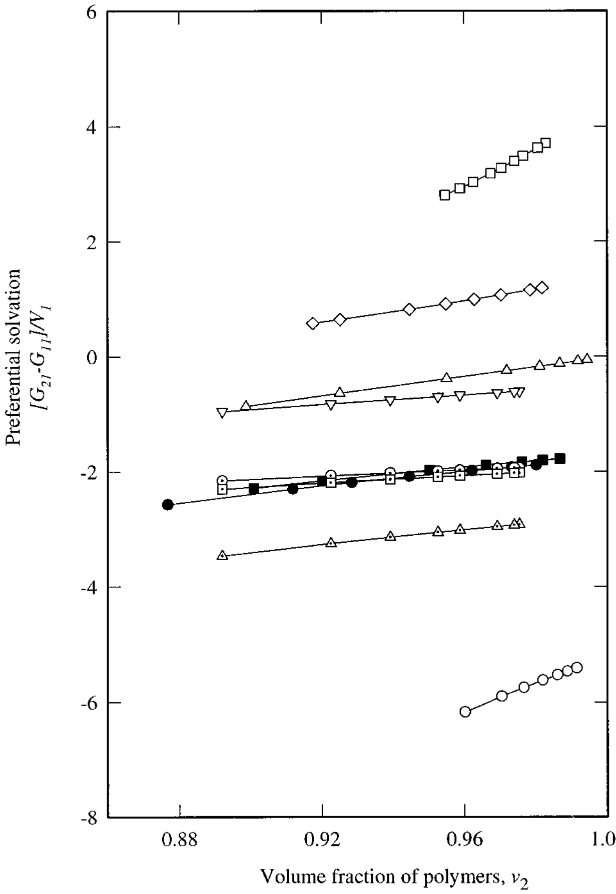

Figure 7. Concentration dependence of preferential solvation for various polymer−solvent systems: (○) PCTTP−*n*-hexane at 50.0 °C; (◬) PDMS−benzene at 25.0 °C (interaction parameters taken from ref 32b); (●) PDEG−SA−toluene at 40.0 °C; (■) PDEG−SA−toluene at 50.0 °C; (⊡) PDMS−cyclohexane at 25 °C (interaction parameters taken from ref 32b); (⊙) PDMS−*n*-hexane at 25.0 °C (interaction parameters taken from ref 32b); (△) PDMS−*n*-hexane at 60.0 °C; (▽) PDEG−SA−toluene at 75.0 °C; (□) PCTTP−CH$_2$Cl$_2$ at 50.0 °C; (◇) PDEG−SA−THF at 75.0 °C.

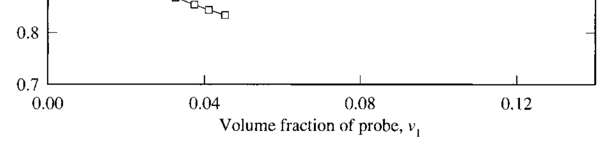

Figure 8. Concentration dependence of mean cluster size for various polymer−solvent systems: (○) PCTTP−*n*-hexane at 50.0 °C; (◬) PDMS−benzene at 25.0 °C (interaction parameters taken from ref 32b); (●) PDEG−SA−toluene at 40.0 °C; (■) PDEG−SA−toluene at 50.0 °C; (⊡) PDMS−cyclohexane at 25 °C (interaction parameters taken from ref 32b); (⊙) PDMS−*n*-hexane at 25.0 °C (interaction parameters taken from ref 32b); (△) PDMS−*n*-hexane at 60.0 °C; (▽) PDEG−SA−toluene at 75.0 °C; (□) PCTTP−CH$_2$Cl$_2$ at 50.0 °C; (◇) PDEG−SA−THF at 75.0 °C.

Solvent Clustering in the Polymers. The synthesis and study of polymers with a main chain constructed from inorganic elements is of increasing interest from both fundamental and applied perspectives because of the unusual physical and chemical characteristics associated with these novel materials. Compared to carbon-based polymers, inorganic polymers may show interesting properties such as enhanced durability in harsh environments or low glass transition temperatures.[39] Material characteristics are influenced by the microscopic structure of the macromolecules in the bulk. To suitably analyze the physical microstructures of the polar PCTTP, a polymer with inorganic elements in the main chain, a polar solvent, CH_2Cl_2, and a nonpolar solvent, *n*-hexane, were used.

The self-cluster integral and the preferential solvation, as well as the mean cluster size, are shown in Figures 6–8 for *n*-hexane and CH_2Cl_2. For the convenience of comparison we plotted the concentration dependence of the self-cluster integrals for some ideal FH media with different χ values at $r = 100$ in shaded lines in Figure 6. The dotted lines for FH media of $\chi = -1$, 0.2, and 1.5 show the size dependence of the self-cluster integral increasing from size $r = 10$ to 100 and to 1000. It is obvious that the size effect becomes steadily smaller as the size itself increases. For instance, from 100 to 1000 the size effect can be barely seen. A larger size produces a stronger intrachain correlation or increase in the clustering of the polymer units and also increases the inhomogeneity in the system, as indicated by the increased changing tendency in the plots of the self-cluster integral. The much larger value of the self-cluster integral of *n*-hexane than of CH_2Cl_2 in PCTTP indicates a strong gathering of the *n*-hexane molecules in the polymer bulk. The MCS indicates an increasing value with the increase of the probe concentration for the PCTTP–*n*-hexane system. MCS decreases for the PCTTP–CH_2Cl_2 system in this concentration regime. *n*-Hexane is a nonpolar solvent; the interaction between this solvent and the polymer is a dispersion force. The penetration of the probe molecules into the polymer proceeds only by the basic osmotic effect from the van der Waals potential. One can see that the concentration dependence of the self-cluster integral of the *n*-hexane–PCTTP system has a smaller slope in absolute value than for the system of CH_2Cl_2–PCTTP. It is interesting to mention that for a poor solvent dispersed into the polymeric medium, one important factor is the free volume distribution, for which description by "hole" fluctuation theory has been attracting attention[40] (see next section).

By disrupting the attraction between polar groups on neighboring chain units, responsible for local structure inhomogeneity, CH_2Cl_2 intimately penetrates the bulk, thus revealing by stages the inherent inhomogeneity. The positive value of the preferential solvation shown in Figure 7 indicates the specific electrostatic interaction between PCTTP and CH_2Cl_2. In addition, the self-cluster integral of CH_2Cl_2 is rather small and veers downward with the decrease of the solvent concentration. This shows the dispersion of the probe molecules and the affinity of the solvent to the polymer. The sharp increase of the self-cluster integral, $G_{11}/\bar{V}_1$, shows the strong density fluctuation due to the polar interaction in the system (see next section). Examining the electron distribution in PCTTP segments provides insight into the notable structural inhomogeneity. In fact, this polymer has a low glass transition temperature, T_g, of −25 °C. Such a low T_g suggests either a good chain flexibility or a weak attractive interaction between chains.

Ab-initio calculations for models of the same backbone polymers [halogenated poly(thionylphosphazenes)] by Jaeger et al.[41] have shown that the torsional barrier for rotations around these bonds ranges from 1.5 to 3.5 kcal/mol. The flexibility of the S–N–P and P–N–P bond angles contributes significantly to the torsional mobility of the PCTTP backbone. These ab-initio calculations also indicate a periodic localization of charge on P–N–P moieties. Hence, electrostatic interaction between chains is expected to occur, and mer–mer complexes form to minimize the intersegmental attraction potential energy. The dipole distribution fluctuates spatially, thus contributing to inhomogeneity. These fluctuations would result in the polar section of the chains being distributed into two different regimes—the dipoles in the core of the complexes and the dipoles between the complexes. The free volume will exist between the complexes as "holes". In this case, a fluctuation in the distribution of the "holes" in lattice or continuous spacing[42–44] may adequately describe the free volume effect on the microstructure. The *n*-hexane essentially probes the parts of the medium that are less polar but are still very polar compared to hydrocarbons. CH_2Cl_2 is a polar solvent with high molecular dipole moment that tends to have strong interactions with polar parts. An increase in the concentration results in an increased penetration of the CH_2Cl_2 in the core part of the mer–mer complexes in the medium. One can prove that there are local concentrations of charge by adding a quaternary ammonium salt, $[Bu_4N]^+Br^-$, to THF solutions of poly[aryloxy(thionylphosphazenes)].[45] Light scattering studies reveal a decrease of hydrodynamic radius on addition of the salt, which indicated a reduction in the electronic dipole repulsion between neighboring segments. Hence, the chain configuration goes from an extended one to a more compact coil. At the same time, the associated UV spectrum of the solution undergoes a red shift on addition of $[Bu_4N]^+Br^-$. The effect of various substituents is to alter the dipole moment due to the localized charges on the backbone. In the case of phenyl substituents, it makes them stronger, which in turn imparts rigidity to the overall chain conformation (and hence enhances T_g). Trifluoromethyl groups or halogen atoms do the reverse. The introduction of strong dipoles of CH_2Cl_2 would greatly relax the intramolecular strain from the electrostatic repulsion of highly polarized parts of the backbone of PCTTP.

As a comparison, PDMS was studied at 60 °C using *n*-hexane as the probe. PDMS–solvent interaction parameters obtained by Price and Guillet[32b] on PDMS with *n*-hexane, cyclohexane, and benzene at 25 °C were used to determine cluster integrals. The values of the self-cluster integrals, $G_{11}/\bar{V}_1$, the preferential solvation, $G_{21} - G_{11})/\bar{V}_1$, and the mean cluster size, MCS, as a function of the volume fraction for the four polymer–solvent systems discussed are shown in Figures 6–8, respectively. Decreasing values of $G_{11}/\bar{V}_1$ refer to a weaker tendency of the solvent molecules to form clusters and thus correspond to an increase in the solvent–polymer miscibility. At a given constant solvent volume fraction, the best solvent for PDMS of the polymer–solvent systems studied is *n*-hexane at 60 °C, which is followed by *n*-hexane at 25 °C, cyclohexane at 25 °C, and benzene at 25 °C. As expected, benzene is the worst solvent and has the greatest tendency to form self-clusters (see Figure 7). All the probes used included C_6 hydrocarbons. The major difference in the probe structures is the shape of the molecules and the electronic structure.

Figure 6 shows that the self-cluster integral increases with the concentration of the probes in the polymer. This corresponds to a picture of a microstructure with more inhomogeneity in its composition upon the increase of the probe molecules in the bulk of the polymer. In particular, benzene shows a stronger concentration dependence in its cluster integral than any of the other solvents for PDMS. Figure 8 shows the increase of the mean cluster size with concentration. The largest increase with concentration was observed for the benzene−PDMS system.

As is well-known, benzene has a round-flat shape and π-electronic structure, which makes the "self-attraction" stronger and more favorable by mutual instant polarization. Cyclohexane and n-hexane have no π-electrons and have different "self-attractions". PDMS has only σ-electrons. The polarity of a polymer can be estimated with the dipole moment of a segment in a chain. Decamethyltetrasiloxane has a dielectric constant of 2.39 and a dipole moment of 1.22 D,[46] which can be compared to the dielectric constant of polyethylene, i.e., 2.3 and the dipole moment of $(C_2H_5)_2O$, 1.22 D.[47] These are the major reasons why the saturated hydrocarbons behave similarly and why they behave differently from benzene (dipole moment is zero based on molecular symmetry) distributed into PDMS. The two systems of PDMS with hydrocarbons behave similarly to an ideal FH medium, indicating a much more even distribution of hydrocarbon molecules in PDMS than of benzene. The distribution of the hydrocarbon molecules in the polymer structure remains almost constant, as seen in Figure 6.

The thermal and rheological properties of various metal-ion-containing polyesters have been the subject of intensive previous research.[48] For the understanding and control of the properties of ion-containing polyesters, information regarding segmental partition and the spatial distribution of solvents is important. For example, during preparation of ion-containing polyesters, solvents such as toluene and benzene were used so that the ionic centers would be well dispersed and a unique structure could be formed after the solvent was eliminated.[35] Hence, we chose the polyester PDEG−SA as another model system for studying clustering.

In FDIGC experiments toluene and tetrahydrofuran (THF) were used as molecular probes. The values of $G_{11}/\bar{V}_1$, $(G_{21} - G_{11})/\bar{V}_1$, and the mean cluster size as a function of the volume fractions for the two polyester−solvent systems discussed are displayed in Figures 6−8, respectively. A comparison of the corresponding $G_{11}/\bar{V}_1$ values for toluene and THF clearly shows that THF has a greater tendency to diffuse into the polymer and get well dispersed. It does not form clusters as the low MCS values indicate in Figure 8. The positive preferential solvation indicates that there is a specific interaction in this system (Figure 7). This specific polar interaction makes the THF molecules stick to the polymer chains. Hence, the free volume is shared by a solvent molecule−mer complex. The curve veering downward indicates that in very dilute conditions the molecules strongly prefer to penetrate the medium of the polymers. By contrast, the $G_{11}/\bar{V}_1$ values for toluene are higher, indicating a stronger clustering of toluene molecules within the polyester matrix. This observation is confirmed by the negative values of $(G_{21} - G_{11})/\bar{V}_1$, which indicate a poor affinity of the solvent to the polymer. With the increase of temperature, the clustering of the toluene is decreased, as shown by the decreased MCS (see Figure 8).

Comparison of the Microstructures in the Polymers Investigated. In this section we compare the 10 polymer−solvent systems of the three polymers, i.e., PDMS, PCTTP, and PDEG−SA, in order to study the different features in their structures as probed with the solvents. Chemically, the first two are polymers with "inorganic" (non-carbon) elements in the main chain, one nonpolar and one polar. The last one, a polymer with an organic backbone, is polar. The miscibility of the solvents and polymers increases from top to bottom in the graph of the self-cluster integrals as the curves shift down in Figure 6.

Listed from high to low, the value of the self-cluster integral decreases: PCTTP−n-hexane (50 °C), PDMS−benzene (25 °C), PDEG−SA−toluene (40−50 °C), PDMS−hexane (25 °C), PDMS−cyclohexane(25 °C), PDMS−n-hexane (60 °C) system, PDEG−SA−toluene (75 °C) system, PDEG−SA−THF (75 °C), and PCTTP−CH_2Cl_2 (50 °C) system. The PDEG−SA−toluene system at 40 and 50 °C and the PDMS−hexane and PDMS cyclohexane systems at 25 °C are quite close to the ideal FH system at $\chi = 0.5$. In comparison, with a close look, one can see that the concentration dependence of the PDEG−SA−toluene system at 40 and 50 °C has a tendency to change. This suggests that toluene experiences more inhomogeneity in PDEG−SA than the probes in PDMS at 25 °C. The PDMS−n−hexane system at 60 °C is close to the $\chi = 0$ system, i.e., an athermal system. The PDEG−SA−THF system is close to the system of $\chi = -1$, which is an exothermal system. However, there is a different changing tendency (the tangent of the plot), which indicates the difference in the bulk inhomogeneity. All of the systems, except for the PCTTP−CH_2Cl_2 and PDEG−SA−THF systems, have curves that are linear or diverging upward from linear. The PCTTP−CH_2Cl_2 and PDEG−SA−THF systems have a concave shape. These two systems exhibit a strong variation in the self-cluster integral, and the preferential solvation becomes positive (see Figure 7). The other three systems have a negative value of the preferential solvation, which indicates segregation of the macromolecules due to the correlation from the polymer chain's covalent connectivity (e.g., PDMS system) or due to the correlation from various physical interactions between mers (e.g., the electrostatic force in PDEG−SA systems) in the polymer chains.

The inhomogeneity in a system can be discussed with respect to the inhomogeneity of the distribution of the mers (or polar groups) due to specific interaction forces and the inhomogeneity from nonrandom distribution of the free volume. For a poor solvent−polymer system, the clustering of the solvent can be interpreted as the filling of the free volume in the bulk of polymers by probe molecules. The nonrandom distribution of the free volume has an important effect on the nonrandom distribution of the probe molecules. On the other hand, a strong self-interaction of probe molecules, such as benzene, would strongly increase the solvent clustering in the clusters formed in the free volume at high concentrations. For solvents having specific affinity to the chain, the self-cluster integral of probes shows the intimate penetration of probes into the bulk.

The plots of the reduced self-cluster integral, G (see eq 9), vs v_1 in Figure 9 show the effect of the heterogeneity in a polymer bulk more explicitly. The changing tendency in such a plot gives the heterogeneity in a polymer structure in terms of available interaction to a probe in the bulk. In contrast to the corresponding FH system, Figures 6 and 9 indicate the large heterogeneity in the microstructure of the PCTTP. One can see that THF experiences a higher heterogeneity than toluene. Such an observation indicates the fluctuation of the polarity in the medium of PCTTP and PDEG−SA. Figure 9 shows a much larger value of $[\partial G/\partial v_1]$ for PCTTP−CH_2Cl_2 than for PDEG−SA−THF. Since the

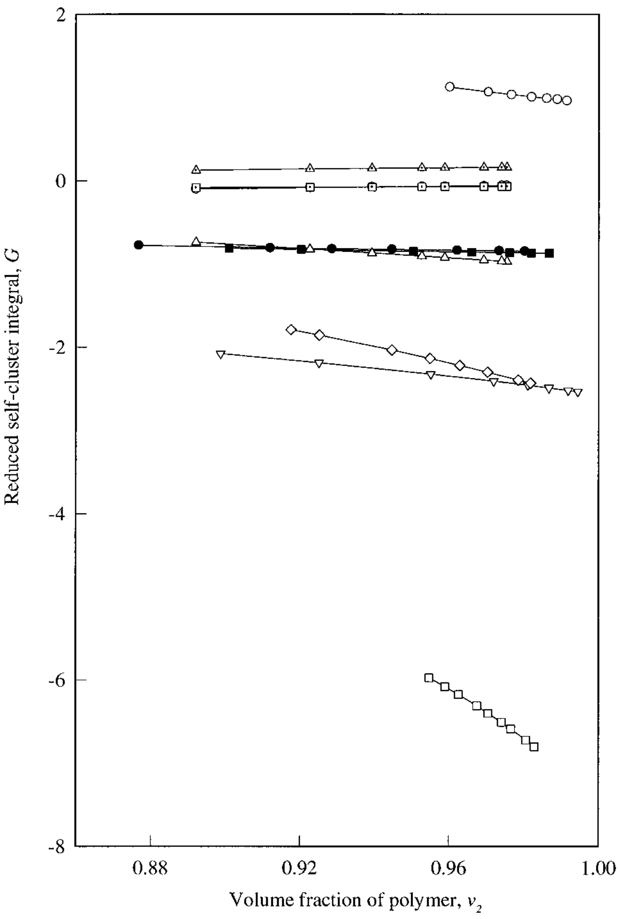

Figure 9. Comparison of recuded self-cluster integrals for various polymer−solvent systems: (○) PCTTP−*n*-hexane at 50.0 °C; (◬) PDMS−benzene at 25.0 °C (interaction parameters taken from ref 32b); (●) PDEG−SA−toluene at 40.0 °C; (■) PDEG−SA−toluene at 50.0 °C; (⊡) PDMS−cyclohexane at 25 °C (interaction parameters taken from ref 32b); (⊙) PDMS−*n*-hexane at 25.0 °C (interaction parameters taken from ref 32b); (△) PDMS−*n*-hexane at 60.0 °C; (▽) PDEG−SA−toluene at 75.0 °C; (□) PCTTP−CH_2Cl_2 at 50.0 °C; (◇) PDEG−SA−THF at 75.0 °C.

CH_2Cl_2 molecules (dipole moment $\mu_d = 17.4$ D)[49] have a polarity similar to that of the THF molecules ($\mu_d = 18.3$ D),[49] the polarity distribution is more inhomogeneous for PCTTP than for PDEG−SA.

Temperature Dependence of Microstructures. The temperature dependence of the microstructure was studied in the good solvent systems, so that the variation of the properties of the probe itself would have only secondary importance when the results were interpreted. The value of the self-cluster integral is reduced when the temperature is increased for all of the PDMS and PDEG−SA systems studied (see Figure 6). This suggests that the probe molecules become more dispersed in the polymer medium and the distribution of the solvent becomes more homogeneous. On the other hand, the concentration dependence of the self-cluster integral becomes stronger when the temperature is increased (see Figure 9). This suggests that the polymer medium becomes more inhomogeneous at higher temperatures.

Higher temperatures essentially enhance the free volume and may reduce the physical interaction between the units in a system. This reduction of the exchange enthalpy enhances the miscibility and reduces the self-cluster integral of the solvent. The mobilities of the mers in chains and of the solvent molecules increase with an increase in the temperature. The change in the rate will be greater for the mers in the chains than for the solvent molecules. This enhances the homogeneity in the composition. However, the small molecules continue to move faster at the same time than the mers in the polymer chains. The solvent molecules will have more free volume than the mers in the chains. Therefore, temperature affects free volume and interaction in opposite ways. The dominant effect is that on the interaction, as shown in Figure 6, and the miscibility is increased.

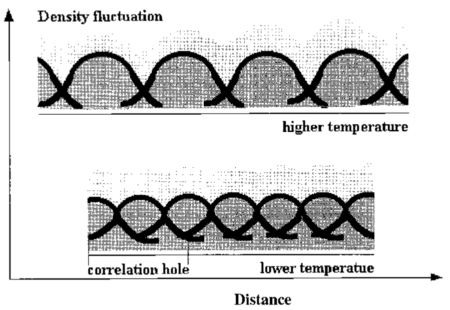

Figure 10. Two-dimensional illustration of the bulk inhomogeneity.

The increase of $\partial G/\partial v_1$ with an increase in temperature shows the effect of free volume. The concentration dependence of the interaction parameter, χ, sweeps from positive to negative for the PDMS−hexane system from 25 to 60 °C. Within this temperature range there exists a temperature where χ does not depend on the concentration and the solution is strictly a Flory−Huggins solution. The *ideal* temperature may vary depending on the properties and the microstructure of different polymers as well as the properties of the probe solvents. As is well established, the macromolecular chains are random chains in its pure amorphous bulk. The mers or units in a chain are correlated with each other by the covalent connectivity. This will create "correlation holes", as pointed out by de Gennes.[8a] The correlation holes will be changed by the introduction of the free volume and mobility of the mers making up the chains (see Figure 10). An increase of free volume will, on the one hand, make the correlation holes more isolated; on the other hand, the higher mobility will make the chain more flexible, which increases the size of the correlation holes and leads to a higher elasticity. The former effect of the free volume dominates so that it makes the medium of the polymers more inhomogeneous. It is worth mentioning that the correlation hole effect has rarely been investigated with thermodynamic experiments. The mean-field analysis has also shown a wider distribution of "vacant sites" with the increase of temperature.[40]

Conclusion

FDIGC can be an efficient tool for studying microstructures in a polymeric material in conjunction with the concept of cluster integrals owing to its capacity for working in a very low concentration regime of the probe. The effects of free volume and the polar and nonpolar interactions as well as the covalent connectivity in a chain on the microstructure of polymers can be explicitly revealed by the changing tendency of the concentration dependence of the self-cluster integral of probes. By use of probes of different natures in interaction force with the polymers, detailed information regarding the physical effect can be investigated. The FDIGC results on

PCTTP, PDMS, and PDEG−SA show that a strong microstructural inhomogeneity can be created due to the polar interactions. The density fluctuation in polymers is enhanced by increasing temperature due to the correlation holes effect.

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