

Light-scattering studies in cross-linked gels: Evidence of a microphase separation

Norberto Micali and Cirino Vasi

Istituto di Tecniche Spettroscopiche del Consiglio Nazionale delle Ricerche, 98166, Vill. S. Agata, Messina, Italy

Francesco Mallamace

Dipartimento di Fisica dell'Università di Messina, 98166, Vill. S. Agata, Casella Postale 55, Messina, Italy

Rama Bansil, Sinisha Pajevic, and Francesco Sciortino

Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215

(Received 8 February 1993)

In this paper we report experimental results from depolarized Rayleigh, Brillouin, and elastic (zero-frequency intensity) scattering, on methyl-methacrylate (MMA) gels cross-linked with ethylenedimethacrylate (EDMA). The study is performed by varying the cross-linking amount of the gels from 0 to 6%. The depolarized Rayleigh scattering is studied in the frequency range 0–150 cm^{-1} while the Brillouin and the zero-frequency intensity data are measured at different scattering wave vectors in the angular ranges 90°–150° and 10°–150°, respectively. The behavior of the measured quantities confirms that in these gels a microphase separation phenomenon takes place. In particular, for samples with cross-linking content higher than 3%, Brillouin data (studied in terms of the group velocity) give information about the existence of well-defined *solidlike* and *liquidlike* islands (heterogeneities in the gel structure) with an extent of several hundred angstroms (as confirmed by elastic-scattering data). Increasing the cross-link concentration in the gel seems to generate an increase in the number of the liquidlike islands, with a reduction in their corresponding size. Depolarized-light-scattering data show (in the same concentration region of EDMA) a change in the freely rotating terminal groups of the MMA polymer.

PACS number(s): 82.70.Gg, 78.35.+c, 61.25.Hq

I. INTRODUCTION

Light scattering is a powerful tool for the study of the structural and dynamic properties of materials. In particular, such studies give information on the translational and rotational motion as well as on the viscoelastic properties due to the interparticle interactions in complex fluid systems, such as supercooled liquids, strongly interacting colloidal solutions, polymers, and gels. As is well known, complex systems contain extended polyatomic structures of length scales larger than atomic and molecular scales, typically of the order of tens of angstroms to several micrometers. Consequently the microscopic properties of these materials are determined by the behavior and organization of the large-scale structures observable on length scales typical of the wavelength of light.

Polarized and depolarized Rayleigh and Brillouin spectra can be used to study collective molecular motion in this class of systems. The information which can be extracted from the measured spectra is mainly related to the translational motion, as reflected by the density correlation function and in the depolarized geometry to the rotational motion of the molecules as influenced by the presence of structural arrangements. Brillouin scattering experiments are useful for the investigation of viscoelasticity in the high-frequency range (GHz). Several Brillouin laser light-scattering experiments have shown that the spectra of polymer solutions are sensitive to the molecular configurational rearrangements and segmental motion

of flexible polymer chains [1–5]. Our objective is to study with this technique the properties of a cross-linked gel for high content (well above the sol-gel transition) of cross-linking molecules. In particular, using polarized Brillouin scattering as a function of the scattered wave vector we analyze the viscoelastic properties of the system in order to have deeper insight into its spatial correlations, while by means of depolarized scattering measurements we study the rotational dynamics of polymer molecules.

At present, great attention is being devoted to the characterization of the structure and dynamics of swollen cross-linked gels because of their fundamental and technological importance in many fields of physics, chemistry, and biology [6,7]. Many theoretical and experimental studies have been performed in order to clarify the structural and dynamical properties of such systems; in particular, viscosity and light scattering have been used for the study of the singularities near the gelation threshold. Quasielastic light-scattering studies have established the existence of a collective diffusional mode with a diffusion coefficient inversely proportional to the hydrodynamic correlation length in the network [8], and also the existence of well-defined viscoelastic properties above and below the gelation threshold [5]. Several authors have studied the dependence of the diffusional modes as a function of several parameters such as concentration, temperature of the gel, and the extent of cross-linking [9].

In comparison to the properties of the gel in the vicinity of the sol-gel threshold, much less is known beyond the

threshold about the scaling behavior, or in general, about many physical properties at high or very high cross-linking content because of complications due to the heterogeneities which may form in the gel. In fact, even in a very good solvent, the branched polymers generated in the cross-linking process will tend to segregate as the number of cross-linking molecules goes beyond the critical percolation point; however, macroscopic segregation is prevented by the existence of the spanning percolating network. As a result, only a microscopic segregation process can take place, with a corresponding building up of localized heterogeneities in the gel structure. This phenomenon, known as microsineresis [7], has been described recently in terms of a percolation model of heterogeneities [10] to describe the clusters of regions with a higher than average cross linking in a randomly cross-linked gel. The regions which are more cross-linked tend to expel the solvent, thus heterogeneities in a cross-link distribution lead to strong variations in the local degree of swelling. Experimental evidence supporting this picture is seen in small-angle neutron scattering [11] of polystyrene and other networks as well as in polyacrylamide gels which become turbid at high crosslink content and show nonmonotonicity in swelling equilibrium and pore-size distributions as the cross-link content is varied. Computer simulations also showed the existence of spatial correlations in the distribution of crosslinking monomers [12], while Raman spectra [13] showed that clusters of the cross-linking monomer appear to form at high cross-link concentration.

Similarly, linear polystyrene incorporated in a styrene-divinyl benzene gel shows phase separation as a function of cross-link content, even though the monomers involved are compatible and miscible [14]. Such phase separation should take place on microscopic scales because the preexisting cross-linking network hinders macroscopic segregation and is a major problem in the fabrication of homogeneous interpenetrating networks.

In this paper, we show that depolarized Rayleigh and Brillouin scattering experiments can be used to probe the dynamics of microphase separated gels, since they are sensitive to the molecular rotational motions and to the viscoelastic changes occurring in the gel network beyond the sol-gel (SG) transition, respectively. While depolarized Rayleigh scattering can give “local” information on the solvent properties in the neighborhood of polymer chains or probe the rotations of the freely rotating terminal groups of the polymer molecules in the gel network [15], hypersound velocity (measured by means of Brillouin experiment) reflects the properties of the collective oscillations of the system. In particular, microphase separation in cross-linked gels would show up in a viscoelastic behavior characterized by a crossover frequency ω (or wave vector k) such that the system can be interpreted as a mainly elastic material for short time and large k and as a viscous fluid for long times and small k . Since the structure and dynamics of such gels are determined by the cross-link content, a question of particular interest is the dependence of the crossover frequency and the crossover wave vector on the cross-link concentration. Similarly the rotational dynamic of solvent and polymer mole-

cules would be sensitive to local variation in cross-linking density and microsineresis. We show that a new length scale, different from the hydrodynamic one, appears in the gel structure for high cross-link concentration. We associate this new length scale to the microscopic segregation process. It should be emphasized that the samples were optically clear, implying that the phase separation process occurs on much smaller length scales than the wavelength of light.

II. EXPERIMENT

The experiments were performed on methylmethacrylate (MMA) gels cross-linked with ethylenedimethacrylate (EDMA) prepared by free radical copolymerization of MMA and EDMA in dioxane (good solvent) with azobisisobutyronitrile as the initiator. Sealed vials containing 12% in volume of MMA plus EDMA in dioxane were polymerized for 80 h in a 50°C bath. The relative amount of cross-linking, defined as f_{EDMA} [the ratio of the volume fraction of EDMA to that of the total monomer (EDMA plus MMA)] was varied from 0% to 6%. The sample with 0% EDMA corresponds to a linear polymer solution of PMMA in dioxane. All other samples were gels, in the region beyond the sol-gel threshold. We also studied the pure solvent (dioxane) and a solution of dioxane-MMA (12% in volume) for comparison. The refractive indices n of the different compounds are, respectively, 1.4165 for dioxane, 1.4549 for EDMA, and 1.414 for MMA. The respective densities are $d = 1.032, 1.051, \text{ and } 0.936$. All data for n and d refer to $T = 20^\circ\text{C}$.

Both the depolarized Rayleigh and Brillouin scattering were measured using a fully computerized double-pass double monochromator (DMDP), SOPRA model no. DMDP 2000, with a half width at half maximum (HWHM) resolution of 700 MHz. For the study of the Brillouin contribution this instrument has an advantage over the Fabry-Pérot interferometer, since we eliminate the problems arising from the periodic boundary conditions. The resolution of the DMDP is comparable to that of a Fabry-Pérot interferometer working at a free spectral range of ~ 50 GHz. The instrument has an exceptionally high stray-light rejection. The depolarized spectra are measured in the frequency range -50 to $+50$ cm^{-1} . In the depolarized geometry we use a resolution of 0.1 cm^{-1} in order to have a higher intensity. The scattering geometry for these experiments is the usual 90° arrangement with the incident beam vertically polarized with respect to the scattering plane. The scattering light was collected through a Glan-Thompson polarizer with an extinction coefficient better than 10^{-7} . The exciting source is the 5145-Å line from an Ar^+ laser (Spectra Physics 2020) operating at an average power of 1 W. All measurements were performed at a constant temperature $T = 17.00 \pm 0.02^\circ\text{C}$, using a thermostated scattering cell with the fluid having the same refractive index as the scattering cell in order to avoid unwanted stray-light effects. The Brillouin scattering was measured at four scattering angles, namely $90^\circ, 115^\circ, 135^\circ, \text{ and } 150^\circ$ (corresponding to scattered wave vectors k at 24.6, 29.5, 32.1,

and $33.6 \mu\text{m}^{-1}$, respectively) using a computerized goniometer. At all the angles studied, the Brillouin peaks are well resolved from the quasielastic zero-frequency contribution. The zero-frequency static light scattering was also measured as a function of scattering angle in the range 20° – 150° (with a resolution of 1°), using the same goniometer and a HeNe laser source operating at 6328 \AA .

A. Depolarized scattering

It is well known that the depolarized light scattering is caused by the fluctuations of the traceless part of the polarizability tensor [16]. The corresponding time correlation function $G^{\text{anis}}(t)$ and its Fourier transform $I_{\text{VH}}(\omega)$ (VH denotes vertical-horizontal) can be characterized by various contributions, which depend on the different mechanisms involved in the scattering processes. Usually the depolarized intensity, or Rayleigh wing, is written in the form

$$I_{\text{VH}}(\omega) = \int_{-\infty}^{\infty} dt e^{-i\omega t} \{ \langle \delta\alpha_{xy}^*(\mathbf{k}, 0) \delta\alpha_{xy}(\mathbf{k}, t) \rangle \times \sin^2(\theta/2) + \langle \delta\alpha_{yz}^*(\mathbf{k}, 0) \delta\alpha_{yz}(\mathbf{k}, t) \rangle \times \cos^2(\theta/2) \}, \quad (1)$$

where $\langle \rangle$ denotes the thermodynamic averaging, $\delta\alpha_{ij}(\mathbf{k}, t)$ indicates the traceless part of the polarizability tensor, and θ is the scattering angle in the usual scattering geometry. In the $I_{\text{VH}}(\omega)$ spectrum, contributions due to the coupling between rotational motion and collective hydrodynamic transport modes are also taken into account. In both the depolarized and Brillouin scattering measurements the high quality of the fit of the data implies that it is not necessary to consider other central ($\omega=0$) components due to relaxation modes [17]. Therefore the observed spectra are characterized by the molecular rotational motion.

The depolarized Rayleigh scattering spectra in such conditions contain mainly two contributions: (i) the far contribution ($\omega \geq 30 \text{ cm}^{-1}$) due to collisional interactions

and the narrow one ($\omega \leq 30 \text{ cm}^{-1}$) caused by molecular rotational motions. As both solvent and polymer molecules of the gel network are composed of anisotropic units, the spectrum of the gel will involve contributions from the different rotating molecular groups. Such contributions are Lorentzian lines related to the exponential time decay of the local order. On this basis, our data were fitted to either a single Lorentzian or a double Lorentzian. As a result of such a procedure we obtain that the pure solvent spectrum is well described by a single Lorentzian plus the instrumental response function, while all the other spectra can be fitted only in terms of two significant contributions. The HWHM and the relative intensity of each Lorentzian are obtained directly by the fitting program. The true HWHM was obtained after subtraction of the instrument response function linewidth. In Fig. 1 we show the results of such fitting procedure, in the frequency range -30 to $+30 \text{ cm}^{-1}$, for the gel with $f_{\text{EDMA}} = 2\%$. Figure 2(a) shows the fitted spectra for pure dioxane and MMA solution in dioxane; the corresponding spectra for the gels with varying cross-linking content, $f_{\text{EDMA}} = 0\%$, 1% , 2% , and 6% are reported in Fig. 2(b). The pure solvent exhibits a HWHM of about 3 cm^{-1} , while the dioxane plus MMA solution, the PMMA solution ($f_{\text{EDMA}} = 0$), and the gels, with different cross-linking contents, show two contributions having a HWHM of about 3 and 18 cm^{-1} , respectively. The faster contribution (HWHM of 18 cm^{-1}) may be related to the rotation of the terminal CH_3 groups [18].

B. Brillouin scattering

The fully polarized scattered intensity vs the frequency ω , at a given k , gives information on the dynamic structure factor $S(k, \omega)$, which is the Fourier transform of the k th component of the density-density correlation function $G_\rho(k, t) = \langle \delta\rho(k, 0) \delta\rho(k, t) \rangle$. The dynamic structure factor depends on the viscoelastic behavior of the system under examination and can be written as [19]

$$S(k, \omega) = A \left\{ B \frac{2D_t k^2}{\omega^2 + D_T k^2} + \frac{1}{\gamma} \left[\left(\frac{\Gamma^2(k)}{[\omega - \Delta\omega(k)]^2 + \Gamma^2(k)} + \frac{\Gamma^2(k)}{[\omega + \Delta\omega(k)]^2 + \Gamma^2(k)} \right) - \frac{\Gamma(k)}{\Delta\omega(k)} \left(\frac{\omega + \Delta\omega(k)}{[\omega + \Delta\omega(k)]^2 + \Gamma^2(k)} - \frac{\omega - \Delta\omega(k)}{[\omega - \Delta\omega(k)]^2 + \Gamma^2(k)} \right) \right] \right\}, \quad (2)$$

with $A = (1/\pi)V\rho^2 k_B T \beta_T$ and $B = (1-\gamma)/\gamma$. Here V is the scattering volume, ρ the system density, k_B the Boltzmann constant, T the temperature, β_T the isothermal compressibility, γ the specific heat ratio, $\Gamma(k)$ the Brillouin linewidth, and $\Delta\omega(k)$ the Brillouin shift. The first term of Eq. (2) represents the zero-frequency quasielastic component while the second term is the Brillouin contribution written as the sum of its symmetric and asymmetric parts.

We fit our spectra to Eq. (2) in order to derive $\Delta\omega(k)$,

which characterizes the viscoelastic behavior of the gel system. Figure 3 shows the calculated $\Delta\omega(k)$ as a function of the scattered wave vector k for samples with different crosslink concentrations ($f_{\text{EDMA}} = 0, 0.01, 0.015, 0.02, 0.04, \text{ and } 0.06$); in the same figure the corresponding data for pure dioxane and for MMA in dioxane are also reported. All data are in the frequency range 5 – 8 GHz and the full lines represent the data fitting with a polynomial regression. As can be seen from the reported data the Brillouin shift increases linearly with increas-

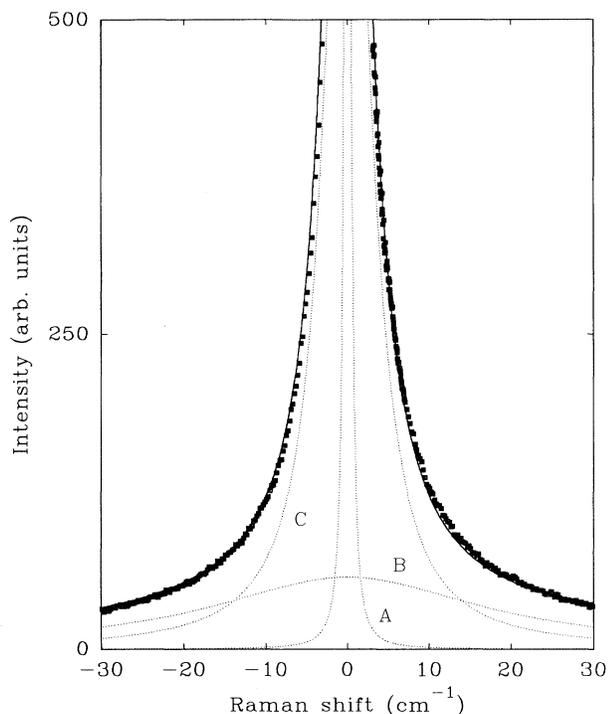


FIG. 1. Details of the fit of the depolarized Rayleigh spectrum, in the frequency range -30 to $+30$ cm^{-1} , of the gel with $f_{\text{EDMA}}=2\%$. The continuous line represents the best fit with the instrumental resolution (curve A) and the two significant physical contributions (curves B and C).

ing wave vector for the linear polymer solution ($f_{\text{EDMA}}=0$) as well as for the gels with a cross-link content less than 1%. For higher concentrations of EDMA molecules we observe two opposite k dependences: for gels with $f_{\text{EDMA}}=1.5\%$ and 2% we find a positive curvature in $\Delta\omega(k)$ vs k while for gels with $f_{\text{EDMA}}=4\%$ and 6% the curvature is negative. From these dispersion curves it is possible to calculate the sound velocity in the medium.

III. RESULTS AND DISCUSSION

The analysis of the observed depolarized spectra performed as described in the preceding section reveals the following general findings.

(i) Only a Lorentzian contribution with a HWHM frequency of about 3 cm^{-1} is present in the data of the pure dioxane.

(ii) All spectra of solutions dioxane-MMA and gels at different cross-link contents are well fitted by two different Lorentzian contributions with HWHM frequencies of about 3 (slow) and 18 cm^{-1} (fast), respectively. For all the samples the HWHM values are essentially the same and therefore independent of the cross-link content.

(iii) While the integrated intensity of the slow Lorentzian is independent of the gel cross-link content, the corresponding value of the fast contribution presents a marked dependence on f_{EDMA} . The integrated intensity values were measured as the area of the corresponding spectral

contributions and are related to the population of the scatterers. Figure 4(a) shows clearly that the integrated intensity I_s of the narrow spectral contribution for the gels is independent of the cross-link concentration. It can also be seen from the figure that the integrated intensity I_s in the gels is the same as that of pure dioxane. Figure 4(b) shows the ratio of the integrated intensity I_f of the broader contribution to the total intensity $\Phi=I_f/(I_f+I_s)$ for the same samples. Here we clearly observe a marked decrease in the population of fast contribution around 4% . To interpret these data we assign the narrow spectral contributions to the rotational dynamics of the dioxane molecules and the broad Lorentzian contribution to freely rotating terminal groups of the MMA methyl side monomer in polymer. In fact, since the MMA molecules are connected in the polymer network, its free rotational dynamics should be characterized by a slower frequency than the observed fast Lorentzian (18 cm^{-1}); hence the only possible contribution to this fast dynamics can come from their freely rotating terminal groups. The comparison with the rotational time obtained by neutron scattering data [18] confirms this interpretation.

The behavior of the fractional number of such scatterers Φ as a function of copolymer content agrees with the picture of a microsineresis in the gel network. An examination of Fig. 4(b) shows first a jump in Φ in the range $0 < f_{\text{EDMA}} < 0.01$, i.e., the region where the system turns from a polymeric solution to a swollen gel; with a further increase in the cross-linking concentration up to $f_{\text{EDMA}}=0.03$ the measured Φ values are nearly constant; just above this concentration value we have a second marked jump in Φ and for larger concentrations ($f_{\text{EDMA}} > 0.04$) Φ remains constant. Such a change in the number of the freely rotating terminal groups of the MMA polymer (Φ) indicates a strong dependence on the structural properties of the system; while the first jump is clearly connected with the SG transition via the percolating structure, the second one is presumably due to the microsegregation phenomenon in the branched polymers of the gel network. The possibility that increasing the cross-link concentration favors a clustering of the polymers [7] can be examined by the analysis of Brillouin data, reported in Fig. 3. As can be seen we have markedly different behaviors in the dispersion curves: negative dispersion above and positive dispersion below $f_{\text{EDMA}} \sim 0.03$ (i.e., in the same region in which we observe the marked jump in Φ). Therefore the behaviors of the two different measured quantities Φ and $\Delta\omega(k)$ have the same origin. We can clarify these results by studying the dispersions curves in terms of both phase V and group V_g sound velocities.

Starting from the original considerations developed by Brillouin [20] we can distinguish among the behaviors of the phase V ($V=\omega/k$) and the group V_g ($V_g=\partial\omega/\partial k$) sound velocities. While V_g represents the forward motion of the average amplitude distribution in the envelope of the "wave packet," V gives details of the single wavelets moving within the envelope. For a medium where V is a constant and does not depend upon the frequency $V=V_g$ and any kind of signal is propagated

without distortion. More generally, for dispersive media (all material media are dispersive) V is function of the frequency $\omega(k)$ and the thermodynamical variables, such as the density ρ and the temperature T . The relation between the group and phase velocities can be written

$$V_g(k) = \frac{\partial \omega(k)}{\partial k} = V(\lambda) + \lambda \frac{\partial V(\lambda)}{\partial \lambda} = V(k) + k \frac{\partial V(k)}{\partial k}, \quad (3)$$

where $k = 2\pi/\lambda$ is the wavenumber. The velocity of sound in condensed materials is approximately constant for large λ , but depends strongly on the frequency at small λ , i.e., when the wavelength is of the same order of magnitude as the characteristic correlation lengths of the system due to well-defined intermolecular interactions or of the correlation range of cluster structures built up by an aggregation or a polymerization process. On this basis

Eq. (3) can explain the structural properties of the dispersive media or their influences on the dynamical modes of the system [20]. In fact, the coupling between the physical system and the probe selects the proper wave vector (or frequency) connected with the peculiar structures and interactions; in Brillouin scattering, such a coupling is reflected into observed quantities as the sound velocity and absorption [21]. In materials comprised of random dispersions of small substructures, i.e., materials in which clustering effects are present, the elastic properties are critically dependent on the connectivity and on the spatial correlations of the constitutive subunits. Therefore the observed viscoelastic properties of a complex fluid, such as polymeric solutions or gels, provide new insights into the spatial correlations and interactions of its components. As an example, for a complex fluid as a gel below the SG transition, there exists, when frequency

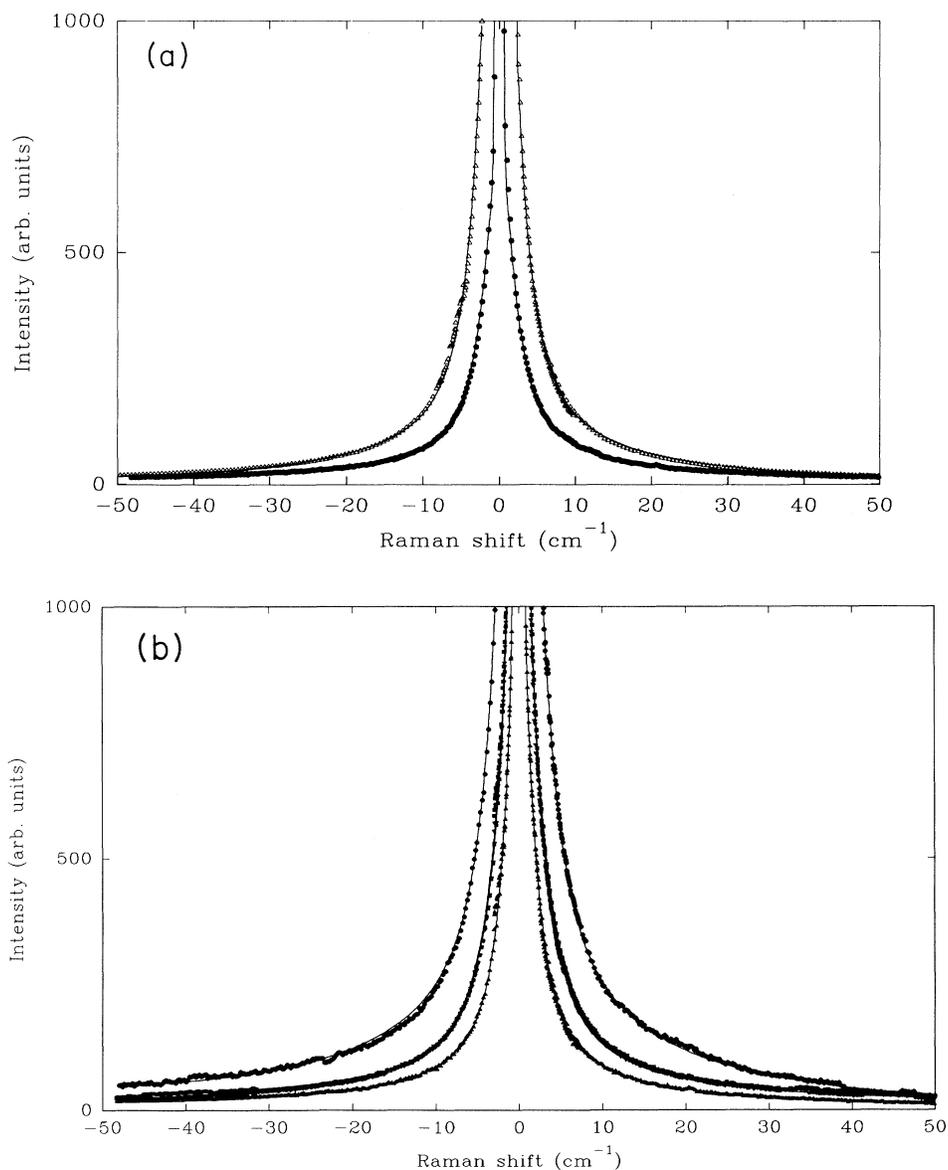


FIG. 2. (a) The fitted depolarized Rayleigh spectra for pure dioxane (dots) and MMA solution in dioxane (triangles). (b) The fitted spectra for gels with different crosslinking content ($f_{EDMA} = 0\%$, 1%, 2%, and 6%). Dots refers to $f_{EDMA} = 0$, full squares and inverted triangles to $f_{EDMA} = 1$ and 2, respectively, and triangles to $f_{EDMA} = 6$.

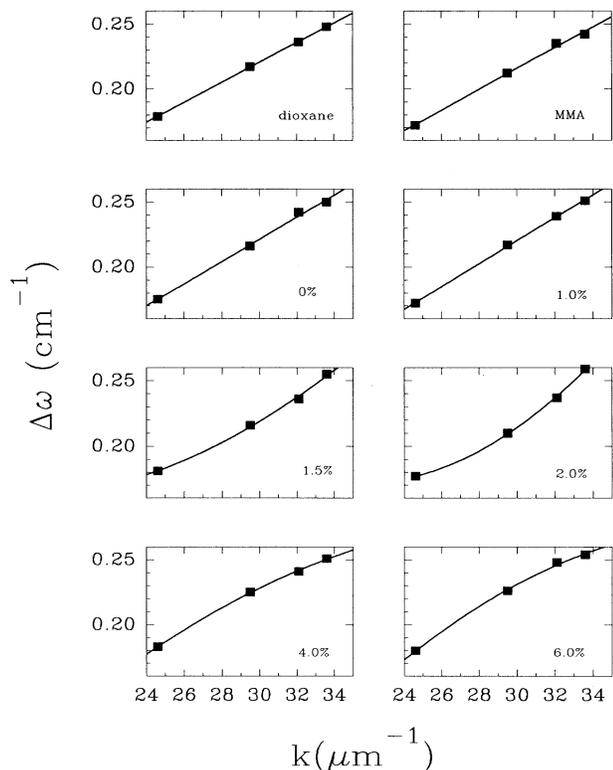


FIG. 3. The Brillouin frequency shift $\Delta\omega(k)$ vs the scattered wave vector k for samples with different cross-link concentrations f_{EDMA} for pure dioxane and for MMA-dioxane solution.

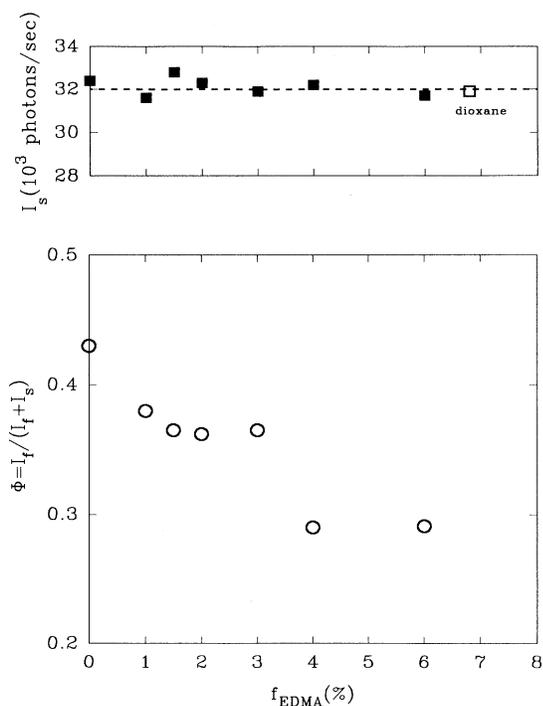


FIG. 4. The integrated intensity I_s (solvent contribution) and the ratio $\Phi = I_f / (I_f + I_s)$ vs the cross-link content f_{EDMA} . I_f is the spectral contribution related to the freely rotating MMS terminal group.

dispersions effects are present, a crossover wave vector (or frequency) such that the behavior of the system can be interpreted as mainly an elastic material for short times and large k and as a fluid for long times and small k .

In an earlier paper [22] we report the phase velocity V , measured from the Brillouin frequency shift values [$V = \Delta\omega(k)/k$], as a function of k for different crosslinked gels and for the unpolimerized solution MMA-dioxane. We observe linear dispersion in the velocity V vs k dependence for dioxane, dioxane-MMA, and samples with cross-link concentrations less than 1%. The comparison of the sound velocities of this low concentrated samples with the velocity value of dioxane indicates coupling between the elastic waves propagating in the polymer network with those propagating in the solvent [3]. Since the density of the different compounds in these gels is nearly the same, we can also consider these velocity data as a measure of the real part of the longitudinal modulus [23]; therefore, in the length scale observable in this experiment we find that the longitudinal moduli of low copolymer content gels are comparable with the bulk modulus of the solvent [24].

Similar data for the phase velocity V vs k for gels with low cross-linking content show a slow decrease up to a minimum located at about $29 \mu\text{m}^{-1}$ for the 1.5% gel and $27 \mu\text{m}^{-1}$ for the 2% gel. For samples with higher contents of cross-linking, we observe maxima instead of minima, located at about $28 \mu\text{m}^{-1}$ for 4% of a cross-linking gel and $31 \mu\text{m}^{-1}$ for gel with 6% cross-linking. We interpret this wave-vector dependence of the extrema by associating the position of the minimum with the characteristic size of the less dense regions, and the position of the maxima with the characteristic size of the highly cross-linked regions in the polymeric network of the gel, due to the microphase separation phenomenon. This interpretation is based on the expectation of a higher (*solidlike*) sound velocity in the highly cross-linked regions and a slower (*liquidlike*) sound velocity in the less cross-linked regions [23,24]. Although the data do not extend over a large k range, the trend in the position of the minimum as a function of k suggests that the size of the less dense regions increases with increasing cross-link content. Correspondingly the characteristic size of the high cross-link regions seems to decrease on increasing the copolymer content. This is consistent with the possibility that increasing the cross-link concentration favors a further clustering of the cross-linked polymers. Since a spanning network is present in the gel, this additional clustering can only be accomplished by an exclusion of the solvent from the already existing clusters, with a corresponding reduction of the cluster sizes and an increasing of the low density liquidlike island in the gel. The difference in concentration between the high and low cross-linked regions increases on increasing the cross-link content. This interpretation agrees with the observed behavior of depolarized Rayleigh light scattering; in the same f_{EDMA} region where we observe this solvent-exclusion phenomenon, we measure a change in the number of freely rotating terminal groups of the MMA polymer.

More definitive information on this phenomenon can

be obtained in terms of the group velocity. As previously discussed, it is the k dependence of the $k[\partial V(k)/\partial k]$ term which quantifies the difference between these two velocities and thus provides additional information on the spatial inhomogeneities in the system. The group velocity V_g obtained from the $\Delta\omega(k)$ data, reported in Fig. 3, as the k derivative of dispersion curves (full curves obtained as a polynomial best-fit to the data) is calculated at the experimental values of the wave vectors:

$$V_g = \left[\frac{\partial \Delta\omega(k)}{\partial k} \right]_{k=k_{\text{expt}}}$$

Figure 5 shows V_g as a function of the cross-link content for the different experimental k values. As can be seen, for the different k_{expt} values, we obtain well-defined minima or maxima in V_g , all centered near $f_{\text{EDMA}} \approx 3\%$, which is the same concentration region in which depolarized Rayleigh scattering data show a jump in the number of freely rotating terminal groups. In particular for the lowest used wave vector $k_{\text{expt}} = 24.6 \mu\text{m}^{-1}$ (scattering angle $\theta = 90^\circ$) we have a minimum in V_g , while for the largest $k_{\text{expt}} = 32.1$ and $33.6 \mu\text{m}^{-1}$ ($\theta = 135^\circ$ and 150°) we have more pronounced maxima; an intermediate situation is found for $k_{\text{expt}} = 29.5 \mu\text{m}^{-1}$, corresponding to $\theta = 115^\circ$. Since the k dependence of the group velocity is mainly due to the contribution $\partial V(k)/\partial k$, it reflects structural effects on a length scale $\xi \sim k^{-1}$. Furthermore, at a given k , a decrease (negative dispersion) in V_g indicates a low-density structure; correspondingly an increase (positive dispersion) in V_g is connected with a more rigid

system. Consequently the observed minima and maxima in $V_g(k)$ reflects, for gels with different f_{EDMA} , mean liquidlike or solidlike behavior, respectively.

Thus the k dependence of phase and group velocities support the proposed interpretation. The k dependence in V_g data shows unambiguously (at least for the cross-link concentration $f_{\text{EDMA}} \geq 3\%$) the additional clustering of the polymers in the gel upon increasing the cross-link contents, accomplished by the solvent exclusion phenomenon from the already existing clusters with a corresponding reduction of the cluster sizes and an increasing of the low-density liquidlike islands size.

From Fig. 5 we observe the following behaviors: for $f_{\text{EDMA}} \leq 1\%$, corresponding to the linear polymer and near the SG transition, V_g is independent of k , indicating a system which is homogeneous on a length scale corresponding to the experimental wave-vector range. With increasing the cross-link content up to $f_{\text{EDMA}} \sim 3\%$ we observe a strong dependence of V_g on k ; its behavior for the lower- k value indicates that the sound propagates on large length scales as if in a liquidlike structure, while for larger- k values, i.e., shorter length scales, the structure appears to be solidlike. This result provides evidence for a system with structural inhomogeneities. The k cross-over value from a liquidlike to the solidlike behavior corresponds to $29.5 \mu\text{m}^{-1}$, from which we estimate the extent ξ of such heterogeneities to be round 300 \AA . This is larger than the hydrodynamic correlation length ξ_c , obtained from quasielastic light-scattering (QELS) measurements [25], but agrees, as we will show in the next section, with zero-frequency light intensity data and a small-angle neutron scattering (SANS) study in the same gels [26].

In the region of higher cross-link contents $f_{\text{EDMA}} > 3\%$ we observe a k behavior of the V_g data that is different, in some way opposite, from those obtained in the range $1\% < f_{\text{EDMA}} < 3\%$; in fact we have that the solidlike behavior is observed from the group velocity data calculated at the lower wave vector ($k_{\text{expt}} = 24.6 \mu\text{m}^{-1}$), while the higher wave-vector values ($k_{\text{expt}} = 32.1$ and $33.6 \mu\text{m}^{-1}$) show a behavior connected with a liquidlike structure. A subsequent increase of the cross-link concentration in the gel seems to generate an increase in the number of the liquidlike islands, with a reduction of the corresponding size, and an increase in the size of the solidlike regions. In these particular samples the solidlike regions, i.e., the regions of gel which are less swollen, actually become larger in size than the more swollen regions as a consequence of clustering of cross-links. This agrees with the results of depolarized Rayleigh scattering.

It is useful for the present discussion to report here the main results of another study [29] concerning the zero-frequency intensity data (in the k range $4.8\text{--}26.8 \mu\text{m}^{-1}$) and their comparison with the general findings of the analysis of SANS measurements [26] performed on the same gels. Due to the complexity and variety of cross-link formation an exact solution for the scattering function from gels has not been proposed. However, starting from the consideration that when cross-links are introduced to the polymer solutions the concentration fluctuations are perturbed due to the cross-linking formation,

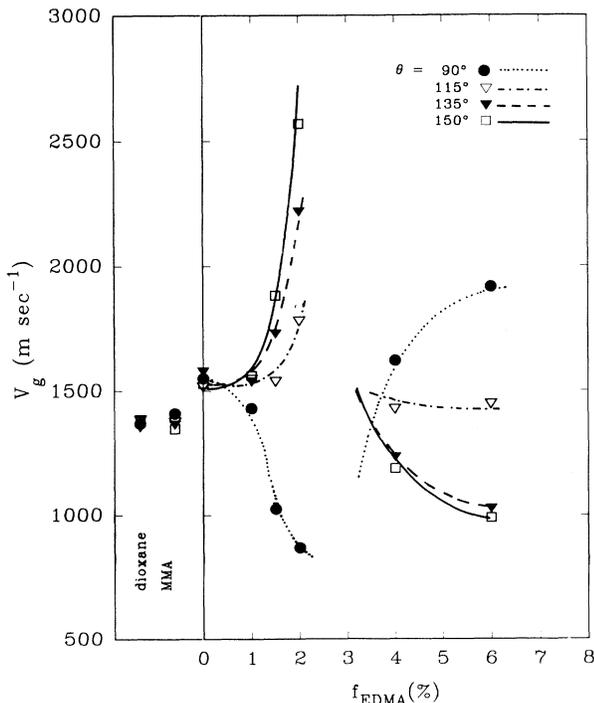


FIG. 5. The group velocity V_g as a function of the cross-link content for the different scattering angles: $\theta = 90^\circ$, 115° , 135° , and 150° .

the scattering function can be assumed to be the sum of two contributions, i.e., *solutionlike* and *solidlike* concentration fluctuations [27]. More specifically, for chemically cross-linked gel systems, the SANS intensity data can be described by a scattering function that is the sum of a Gaussian part (which is the same as the Guinier function) plus a Orenstein-Zernike term [28]. The Gaussian part is considered to result from the built-in inhomogeneity due to the cross-link formation. On the basis of the very different accessible k ranges with neutron and light-scattering experiments, we cannot use such a scattering function to study our light intensity data for gels. In particular, our static structure factors $I(k)$ are represented by a nearly constant behavior for the wave-vector region corresponding to the angular range 60° – 150° while for lower wave vectors we have a large- k -dependent contribution. We study this zero-frequency light-scattering result considering a scattering function in terms of the scattering model proposed for SANS data. Taking into account the results of the Brillouin scattering, $k\xi < 1$, the SANS Gaussian contribution can be approximated, in the k range corresponding to light scattering, to the constant background observed in the present experiment, while the extra term in the intensity, at low wave vectors, is fitted by a Lorentzian form. We suggest that this contribution is related to fluctuations originated by the heterogeneities. For the present study the values of the amplitudes of the above-mentioned terms obtained at different cross-link concentration are of main relevance; the Lorentzian amplitude $I_L(k=0)$ is given by the scattered intensity at zero wave vector after the subtraction of the Gaussian contribution I_G .

In Fig. 6 we report the values of the scattered intensity at zero wave vector $I_L(k=0)$, obtained by extrapolation to $k=0$ (by means of the fitting scattering function) of the scattered intensity measured at the different k values. $I_L(k=0)$ values are shown as functions of the cross-linking content (f_{EDMA}) and the values corresponding to the pure dioxane and the MMA-dioxane solution are also reported for comparison. The inset represents the scattered intensity due to the contribution I_G vs f_{EDMA} . As can be seen, we have a strong increase in $I_L(k=0)$ in the same range of EDMA concentrations in which we observe the microphase separation phenomenon; for higher cross-linking concentrations we observe a decrease in the $I_L(k=0)$ up to $f_{\text{EDMA}}=6\%$, where the measured value is about the same percent of the MMA-dioxane solution. Such a structural picture is the same shown from hyper-sound data (group velocity) and depolarized light scattering. Additional confirmation on the proposed structural picture can be obtained from the comparison of I_G with the SANS data at different f_{EDMA} . The observed monotonic increase (inset of Fig. 6) of I_G with f_{EDMA} is nearly the same one observed by SANS. This represents an additional indication of the microphase separation in cross-linked gels [26].

IV. CONCLUDING REMARKS

We have studied the properties of swollen gels for different crosslinking content, well above the SG transi-

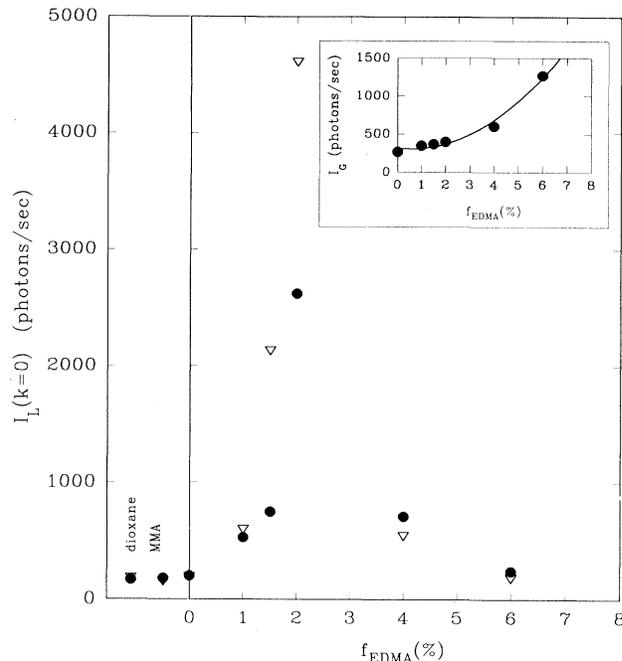


FIG. 6. The zero-wave-vector scattered intensity values $I_L(k=0)$ as a function of the cross-linking content (the two symbols represent two measurements in the same experimental conditions). Also shown are the data for pure dioxane and the MMA-dioxane solution. Reported in the inset is I_G , the nearly constant background contribution.

tion, by means of different light-scattering techniques (elastic, Brillouin, and depolarized Rayleigh) in order to get information about the structural properties of such complex systems. The results are consistent with the possibility that at a new “critical” concentration the gel undergoes a phase separation triggered by increased cross-link content. This phase separation is frozen in by the presence of the already existing spanning network, explaining the observed microscopic k scale. Because light-scattering measurements can be used successfully to detect such microscopic inhomogeneity or their effects on the system dynamics, we performed experimental studies on both the Brillouin shift at different scattered wave vector and the diffusional rotational dynamics of the gels.

In summary, our measurements give a detailed account of the microsegregation process in the system, driven by increasing the content of the cross-linker. Our results support the picture of heterogeneities produced in the gel; high cross-link content favors a further clustering of the polymers and leads to exclusion of the solvent from the already existing clusters. The analysis of the depolarized Rayleigh scattering spectra, in terms of two different contributions due to the rotational dynamics of the solvent and the terminal groups of polymer molecules, respectively, gives direct information that the process is essentially due to the interactions between polymer and copolymer molecules of the structural network. Over the frequency range examined here, the rotational dynamics of the solvent molecules is insensitive to the changes in

the structure while we observe a marked change in the number of freely rotating terminal groups of the MMA polymer both below the SG transition and at the critical cross-linking concentration for which we observe the network microsineresis ($f_{\text{EDMA}}=3\%$). The wave-vector dependence of the Brillouin shift data, showing different behaviors in the dispersion curves, confirms this interpretation.

The behavior of the phase and group velocities of hypersound as functions of the scattered wavevector for gels with different cross-link content gives details of the proposed picture. The wave-vector dependence of the hypersound group velocity $V_g(k)$ is particularly sensitive to the structural properties of the system and can be distorted by the presence of heterogeneities. Such distortions, originated by the absorbing properties of the medium, are strongly frequency dependent and therefore reflect the dynamics and structural behavior of the physical system. From the obtained V_g data as functions of the cross-linking content and for different experimental wave-vector values, it is clear that in MMA gels the increasing implantation of cross-links produces heterogeneities. Well above the percolation threshold we observe the presence in the gel of liquidlike inhomogeneities whose characteristic size increases with the cross-link contents

up to a concentration of copolymers molecules of about 3%. The estimated values of the sizes of such less dense regions are of the same order of magnitude as those obtained by QELS measurements. Further increasing the cross-link concentration in the gel seems to generate an increase in the number of the liquidlike islands, with a reduction in their corresponding size.

This structural picture has been confirmed by elastic light-scattering data and by the comparison with SANS results; in particular the values of the scattered intensity at zero wave vector $I(k=0)$, a quantity directly connected with the system compressibility, show a well-defined maximum for $f_{\text{EDMA}} \sim 3\%$. Finally, we conclude with the observation that the microsineresis process in highly cross-linked gels is well described by different light-scattering experimental techniques, i.e., elastic, QES, depolarized Rayleigh, and Brillouin.

ACKNOWLEDGMENTS

We wish to thank H. E. Stanley for helpful discussions. The research at Boston University was supported by grants from the NSF. The research by F.M. was supported by MURST and CNR.

-
- [1] Y. Y. Huang, C. H. Wang, *J. Chem. Phys.* **64**, 4748 (1975); Y. H. Lin and C. H. Wang, *ibid.* **69**, 1546 (1978); C. H. Wang, *ibid.* **95**, 3788 (1991).
- [2] G. Fytas, Y. H. Lin, and B. Chu, *J. Chem. Phys.* **74**, 3131 (1981).
- [3] J. A. Marqusee and J. M. Deutch, *J. Chem. Phys.* **75**, 5239 (1981).
- [4] E. Kato, *J. Phys. Soc. Jpn.* **56**, 1779 (1987).
- [5] See, e.g., J. E. Martin and J. Wilcoxon, *Phys. Rev. Lett.* **61**, 373 (1988).
- [6] J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1970).
- [7] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).
- [8] Tanaka L. O. Hocker, and G. Benedek, *J. Chem. Phys.* **59**, 5151 (1973).
- [9] See, e.g., A. M. Hecht and E. Geissler, *J. Phys. (Paris)* **39**, 631 (1978).
- [10] J. Bastide and L. Leibler, *Macromolecules* **21**, 2647 (1988).
- [11] F. H. Zielinski, M. Buzier, C. Lartigne, J. Bastide, and F. Boué, *Prog. Colloid Polym. Sci.* **89**, 107 (1992).
- [12] R. Bansil, M. Willings, and H. J. Herrmann, *J. Phys. A* **19**, L1209 (1986).
- [13] K. Gupta and R. Bansil, *J. Polym. Sci.* **21**, 969 (1983).
- [14] M. Briber and B. J. Bauer, *Macromolecules* **24**, 1899 (1991), and references therein.
- [15] G. Fytas, A. Rizos, G. Floudas, and T. G. Lodge, *J. Chem. Phys.* **93**, 5096 (1990).
- [16] B. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976).
- [17] R. Mountain, *Rev. Mod. Phys.* **38**, 205 (1966); C. J. Montrose, V. A. Solov'yev, and T. A. Litovitz, *J. Acoust. Soc. Am.* **43**, 117 (1968).
- [18] F. J. Beruljo, F. Batallon, E. Enciso, R. White, A. J. Dianoux, and W. S. Mowels, *J. Phys. Condens. Matter* **2**, 1301 (1990).
- [19] A. B. Evans and J. G. Powels, *J. Phys. A* **7**, 1944 (1974); G. Maisano, P. Migliardo, F. Aliotta, C. Vasi, F. Wandersingh, and G. D'Arrigo, *Phys. Rev. Lett.* **52**, 1025 (1984).
- [20] L. Brillouin, *Wave Propagation and Group Velocity* (Academic, New York, 1960).
- [21] I. L. Fabelinskii, *Molecular Scattering of Light* (Plenum, New York, 1968).
- [22] F. Mallamace, N. Micali, C. Vasi, R. Bansil, S. Pajevic, and F. Sciortino, *J. Phys. (Paris) II* **2**, 2081 (1992).
- [23] T. A. Litovitz and C. M. Davis, in *Physical Acoustics*, edited by P. Mason (Academic, New York, 1965), Vol. II, Pt. A, Chap. 5.
- [24] L. Ye, D. A. Weitz, P. Scheng, S. Bhattacharya, J. S. Huang, and M. J. Higgins, *Phys. Rev. Lett.* **63**, 263 (1989).
- [25] S. Pajevic, R. Bansil, and C. J. Konac, *J. Non-Cryst. Solids* **131-133**, 630 (1991); *Macromolecules* (to be published).
- [26] J. Bastide, R. Bansil, and F. Boué, *Macromolecules* (to be published).
- [27] A. M. Hecht, R. Duplessix, and E. Geissler, *Macromolecules* **18**, 2167 (1985).
- [28] F. Horkay, A. M. Hecht, S. Mallam, E. Geissler, and A. R. Rennie, *Macromolecules* **24**, 2896 (1991); **24**, 543 (1991).
- [29] N. Micali, C. Vasi, F. Mallamace, R. Bansil, S. Pajevic, and F. Sciortino (unpublished).