*Macromolecules* **1994,** *27,* 917-922

# Density and Concentration Fluctuations in Plasticized Poly(cyclohexyl methacrylate) As Studied by X-ray Diffraction

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*Received July 26, 1993; Revised Manuscript Received November 12, 1993*[●]

ABSTRACT: Small-angle X-ray scattering (SAXS) and pressure-volume-temperature (*PVT*) measurements are employed in bulk and plasticized poly(cyclohexyl methacrylate) (PCHMA) in the temperature range 252-448 K and provide a way of separating the density from the concentration fluctuations. We show that the density fluctuations are suppressed in the mixtures and that the concentration fluctuations increase with plasticizer content. Rayleigh-Brillouin scattering was also employed on the same mixtures, and the contribution of propagating density fluctuations (phonons) to the total fluctuations was evaluated at $T$ above and below the glass transition temperature $T_g$. The excess intensities in the light scattering (LS) and SAXS studies of bulk PCHMA make necessary the introduction of two additional Landau-Placzek ratios, not treated by conventional theories of the liquid state.

## Introduction

It is now recognized that small-angle X-ray scattering (SAXS) directly provides the density fluctuations in amorphous[1-5] or semicrystalline polymers.[6,7] In particular, these studies provided valuable insight into the state of order of amorphous polymers and to the nature of glass formation. In our previous paper,[8] we reported the results of SAXS and specific volume (*PVT*) measurements of two polycarbonates of bisphenol A with a slightly different structure, and we concluded that it is the difference in the packing of chains which causes the differences in the average free volume and in its fluctuations. In this work, we extend the study to include concentration fluctuations in addition to density from a polymer/additive system.

In a one-component system, the fluctuation of the number of particles $N$ in a volume $V$ is given by

$$\langle \delta N^2 \rangle = k_B T \left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} \tag{1}$$

where $\mu$ is the chemical potential. Then, the fluctuation in density in an arbitrary volume is defined as

$$\Psi_T = \frac{\langle \delta N^2 \rangle}{\langle N \rangle} = \rho k_B T \beta_T(T) \tag{2}$$

where $\rho$ is the average number density and $\beta_T$ is the isothermal compressibility ($= -1/V(\partial V/\partial P)_T$). According to eq 2, the density fluctuations should have a temperature dependence similar to that of $\beta_T(T)$, which is discontinuous at $T_g$. However, it has been shown earlier[1-3] that it is only the temperature coefficient of the density fluctuations which is discontinuous at $T_g$.

The density fluctuations defined above can be obtained experimentally in two ways: (i) from the isothermal compressibility measured in a *PVT* experiment (eq 2) and/or (ii) from SAXS, using the extrapolated intensity at $Q = 0$ ($Q = (4\pi/\lambda) \sin \theta/2$, $\lambda$ is the wavelength of X-rays and $\theta$ is the scattering angle) by

$$\frac{\langle \delta N^2 \rangle}{\langle N \rangle} = \frac{I(0)}{nZ} \tag{3}$$

where $n$ is the average electron density and $Z$ is the number of electrons per particle ($I(0) = n^2 k_B T \beta_T$).

The evaluation of density fluctuations using eqs 2 or 3 conceals the relative contribution of propagating and static components in the measured total density fluctuations. To overcome this difficulty we can evaluate the contribution of the propagating density fluctuations from the temperature dependence of the phonon peak obtained in the Rayleigh-Brillouin experiment. This is based on the notion that the propagating density fluctuations are determined from the thermal-diffuse scattering (TDS) near the origin of the reciprocal space, as in the case of crystalline solids.[9] Then, in the limit $Q \rightarrow 0$, this contribution is given by[3,9]

$$\Psi_S = \left. \frac{\langle \delta N^2 \rangle}{\langle N \rangle} \right|_{\text{phonon}} = \rho k_B T \beta_S(T) \tag{4}$$

where $\beta_S(T)$ is now the adiabatic compressibility ($\beta_S = 1/\rho^* u^2$, $\rho^*$ is the mass density and $u$ is the sound velocity) evaluated at the frequency $\omega_{\text{phonon}}$.[10] The ratio of the total to the propagating fluctuations defines an "X-ray" Landau-Placzek ratio:

$$R_{LP} = \frac{\Psi_T}{\Psi_S} - 1 = \frac{\beta_T}{\beta_S} - 1 \tag{5}$$

which is readily obtained in a Rayleigh-Brillouin experiment from the intensities of the central ($I_C$) and shifted Brillouin lines ($I_B$) as $I_C/2I_B$.

In a two-component system with $N_1$, $N_2$ number of particles and $\mu_1$, $\mu_2$ chemical potentials, the fluctuation in the number of particles $N_1$ is given, in analogy to eq 1, by:

$$\langle \delta N_1^2 \rangle = k_B T \left( \frac{\partial N_1}{\partial \mu_1} \right)_{T,V,\mu_2} \tag{6}$$

and

$$\langle \delta N_1 \delta N_2 \rangle = k_B T \left( \frac{\partial \langle N_2 \rangle}{\partial \mu_1} \right)_{\mu_2,T,V} = k_B T \left( \frac{\partial \langle N_1 \rangle}{\partial \mu_2} \right)_{\mu_1,T,V} \tag{7}$$

Therefore, the fluctuations in the concentrations of the two components are, in general, correlated. Following statistical mechanics calculations,[11] we can introduce the volume and the relative composition fluctuations as new variables:

$$\frac{\delta V}{V} = \frac{u_1 \delta N_1 + u_2 \delta N_2}{V} \tag{8}$$

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[●] Abstract published in *Advance ACS Abstracts,* January 1, 1994.

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and

$$\frac{\delta c}{c} = \frac{\delta N_2}{N_2} - \frac{\delta N_1}{N_1} \tag{9}$$

where $u_i$ (= $\partial V/\partial N_i)_{T,P,N_j}$ is the partial molar volume and $c$ is defined as the relative composition $c = N_2/N_1$. With this definition, the new variables are orthogonal ($\langle \delta V \delta c \rangle = 0$) and therefore, the scattered intensity in the forward direction $I(Q = 0)$ contains two independent contributions: one is the volume (density) fluctuations at constant composition and the other is the concentration fluctuation at constant particle density:

$$\lim_{Q \to 0} I(Q) = \langle n^2 \rangle \Psi + \Delta n^2 C \tag{10}$$

where $\langle n \rangle$ ($= n_1\phi_1 + n_2\phi_2$) is the average contrast for density fluctuations, $\Delta n$ ($= n_2 - n_1$) is the contrast for concentration fluctuations, and $\Psi$ and $C$ are defined in ref 12.

The separation of density from concentration fluctuations although mathematically possible has created a lot of confusion for experimentalists. A way to circumvent the difficulty caused by the presence of both types of fluctuations in mixed systems is to use systems which have zero contrast for concentration fluctuations.[12] In this way only density fluctuations contribute to the scattered intensity. However, only few systems are free from scattering contrast and in the vast majority of systems both fluctuations exist. For polymer blends, incompressibility is usually assumed (zero density fluctuations).[13] For polymer solutions, different length scales were thought to provide a possibility for such separation.[14] However, it is desirable to separate the two contributions without any assumption on the length scales involved.

The purpose of the present study is two-fold. First, to provide an effective and free of assumptions way of separating density from concentration fluctuations and second, to evaluate the contribution of the propagating density fluctuations to the total measured fluctuations on the same system. For the first study we have used SAXS and *PVT* on the polymer/additive system poly(cyclohexyl methacrylate)/dioctylphthalate (PCHMA/DOP). From *PVT* we obtain the density fluctuations whereas the SAXS intensities contain contributions from both types of fluctuations. Density and concentration fluctuations were found to exhibit $T$ and $c$ dependence. Furthermore, we compare the intensities for the density and concentration fluctuations with the intensities associated with the dynamics of the two processes on the same system (ref 15). For the second study, we have evaluated the contribution of propagating density fluctuations from the temperature dependence of the phonon peak obtained in the Rayleigh–Brillouin experiment below and above $T_g$. We find that the propagating density fluctuations increase with $T$ without displaying a discontinuity at $T_g$. Furthermore, the intensities observed in the LS and SAXS $Q$-range were in excess of the predictions from the isothermal compressibility (eq 2).

## Experimental Section

**Samples.** The bulk and plasticized PCHMA samples were prepared by thermal polymerization (Röhm, Darmstadt), with a weight-averaged molecular weight $M_w \sim 2 \times 10^5$. The glass transition temperatures $T_g$, measured with a DSC at a heating rate of 10 K/min were 374, 345, and 319 K for the bulk and the plasticized PCHMA with 10 and 20% DOP, respectively. The samples are identical with those used in the light scattering study of ref 15.

**SAXS Measurements.** The small-angle X-ray scattering measurements were made with a Kratky Compact camera (A. Paar KG) using a slit collimation, as described in ref 8. Measurements were made in intervals of 10 K within the range 303–448 K for the bulk polymer and within the range 252–443 K for the plasticized polymers. The temperature stability was better than ±0.2 K. Data treatment involves corrections for absorption, background scattering, and slit-length smearing.[16] Primary beam intensities were determined by the moving slit method. The determination of the extrapolated value of the intensity at $Q = 0$ was carried out from a plot of ln $\tilde{I}(Q)$ versus $Q^2$, where $\tilde{I}(Q)$ is the slit-smeared intensity. Figure 1 shows the slit-smeared intensities of PCHMA at temperatures above, near and below $T_g$. Figure 2 compares the slit-smeared intensities of the bulk and plasticized polymer with 20% DOP at temperatures equidistant from their $T_g$'s. It is worth noticing, with respect to Figures 1 and 2, the linearity of the data over a broad $Q$-range, which has been observed with most of the amorphous polymers studied in our laboratory. Glass-forming liquids, however, show only a weak $Q$-dependence of the scattered intensity and this difference is currently under investigation.

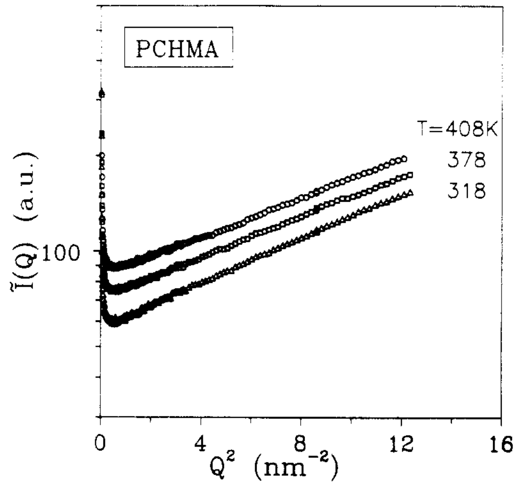

**Figure 1.** Slit-smeared intensities $\tilde{I}(Q)$ for PCHMA at three temperatures; below (318 K), near (378 K), and above (408 K) $T_g$.

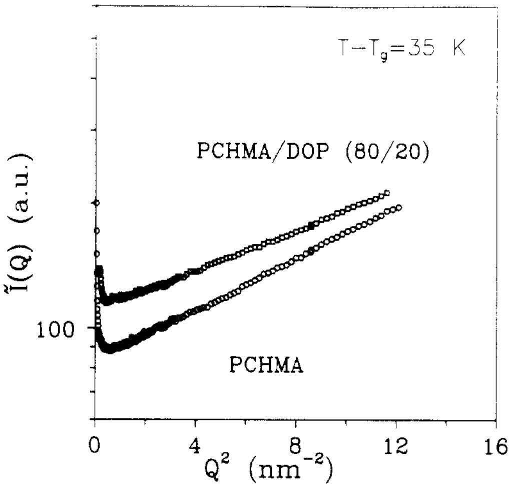

**Figure 2.** Slit-smeared intensities $\tilde{I}(Q)$ for bulk and plasticized PCHMA at $T - T_g = 35$ K. Notice the higher $\tilde{I}(Q)$ for the plasticized polymer.

**PVT Measurements.** The *PVT* measurements on the bulk and plasticized PCHMA were made with a pressure dilatometer (GNOMIX) for pressure intervals of 10 MPa up to 200 MPa. Data were taken isothermally in the temperature range 300–440 K with a stability of ±0.2 K. Figure 3 shows the specific volume data in the form of isobars at intervals of 20 MPa. The glass transition is indicated by the break in the $V(T)$ curve and agrees with the DSC measured value. Vertical and curved lines denote the zero-pressure and the pressure-dependent glass transition, respectively. The *PVT* data of PCHMA shown in Figure 3a are in good agreement with those in ref 17. The isothermal

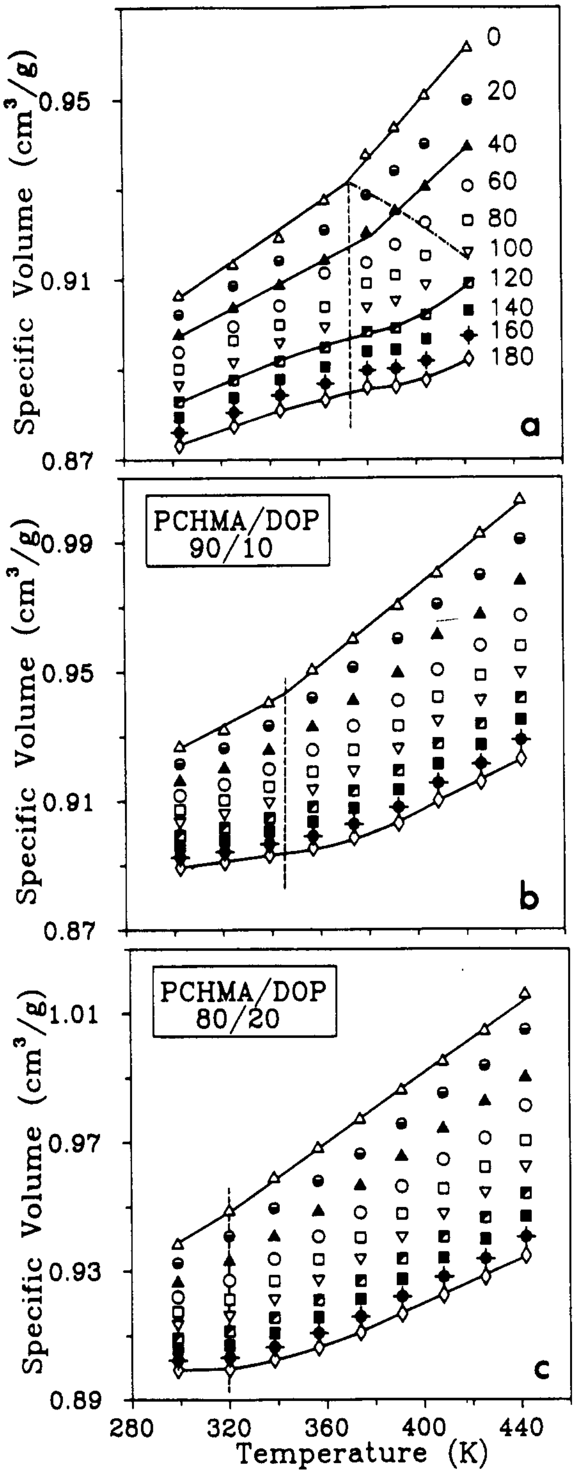

**Figure 3.** PVT data in the form of isobars for (a) bulk and plasticized PCHMA with (b) 10% and (c) 20% DOP, shown in intervals of 20 MPa.

compressibility $\beta_T$ was obtained from the Tait equation:

$$V(P,T) = V(0,T)\left[1 - 0.0894 \ln\left(1 + \frac{P}{B(T)}\right)\right] \qquad (11)$$

which provides an empirical mathematical representation of the PVT data. $B(T)$ in eq 11 is the Tait parameter which is evaluated at each temperature and is related to $\beta_T$ by: $\beta_T(T) = 0.0894B(T)^{-1}$.

**Light-Scattering Measurements.** The Rayleigh–Brillouin measurements were made at a scattering angle of 90°. The light source was an Argon-ion laser (Spectra Physics, Model 2020) operating at a single mode at 488 nm with a stabilized power of 100 mW. The incident and scattered beams were polarized vertically with respect to the scattering plane. The frequency scanning device was a piezoelectrically driven Fabry–Perot interferometer (Burleigh RC-110) stabilized with a Burleigh DAS-10 system. Spectra were taken at a free spectral range of 25.3 GHz with a finesse better than 60. Measurements were made in the temperature range: 229–493 K. The hypersonic velocity, $u$, was calculated from the Brillouin shift $f_B$ and the amplitude of the wavevector $q^*$ (= $(4\pi n/\lambda)\sin \Theta/2$), with $n$ being the refractive index of the medium, by:

$$u = \frac{2\pi f_B}{q^*} \qquad (12)$$

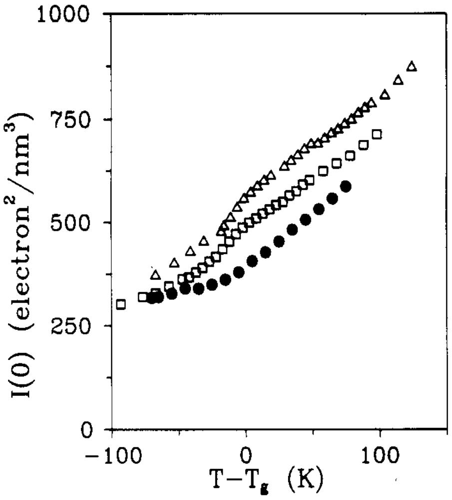

**Figure 4.** Desmeared intensities $I(0)$ for bulk (●) and plasticized PCHMA with (□) 10% and (△) 20% DOP as a function of $T - T_g$.

## Results and Discussion

The scattered intensity for the polymer/additive mixtures is considerably higher from the bulk polymer, when compared at $T$ equidistant from their $T_g$'s (Figure 2). This increase in $\tilde{I}(Q)$ is due to concentration fluctuations present in the former systems. It is worth noticing with respect to Figure 2, that, concentration fluctuations contribute not only to the scattered intensity at small $Q$ (forward scattering) but also at higher $Q$ within the $Q$-range shown. This implies that a separation based on the assumption of different length scales for the density and the concentration fluctuations is not justified.

Subsequently, we have evaluated the temperature dependence of the extrapolated intensity $I(Q = 0)$ using eq 3 for the bulk and plasticized polymer. The result is shown in Figure 4 where $I(0)$, in absolute units, is plotted versus $T - T_g$, making a comparison meaningful. The break in the $T$-dependence of $I(0)$ for PCHMA is consistent with the findings from other polymers[1-8] and glass-forming liquids.[18] It is the result of the nonequilibrium structure below $T_g$. This effect, however, is smeared-out in the plasticized polymers due to the broader transition range also seen in the DSC and PVT measurements (Figure 3b,c). Above $T_g$, the increase of the intensity of the plasticized polymers with respect to the bulk PCHMA is caused mainly by concentration fluctuations. However, this additional intensity cannot be evaluated simply by subtracting from that of the bulk PCHMA because this would assume identical density fluctuations in the bulk and plasticized samples. In fact, it has been shown earlier[12] with respect to some polymer/additive mixtures that density fluctuations may be suppressed provided that the mixed system is free of scattering contrast for concentration fluctuations ($\Delta n = 0$ in eq 10). For this reason, we have evaluated the density fluctuations from the measured compressibilities using eq 2. We have then converted the intensities into fluctuations by using eq 3. The combined SAXS and PVT results are shown in Figure 5, as a function

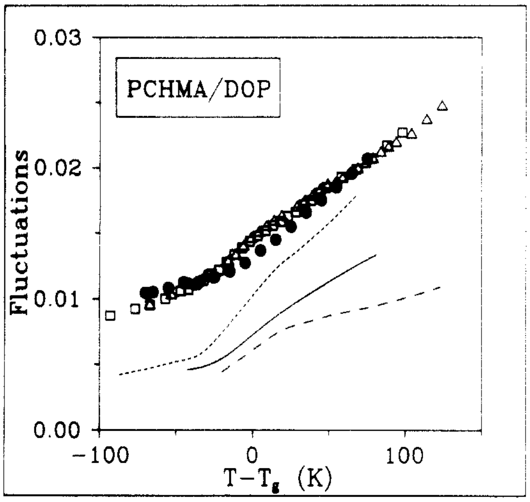

**Figure 5.** Total fluctuations for PCHMA and PCHMA/DOP mixture as a function of $T - T_g$. Data points indicate the total fluctuations (density and concentration) measured by SAXS (eq 3) and capture of Figure 4. Lines indicate the density fluctuations calculated from the isothermal compressibilities (eq 2), (- - -) PCHMA, (—) PCHMA/DOP (90/10), (– –) PCHMA/DOP (80/20).

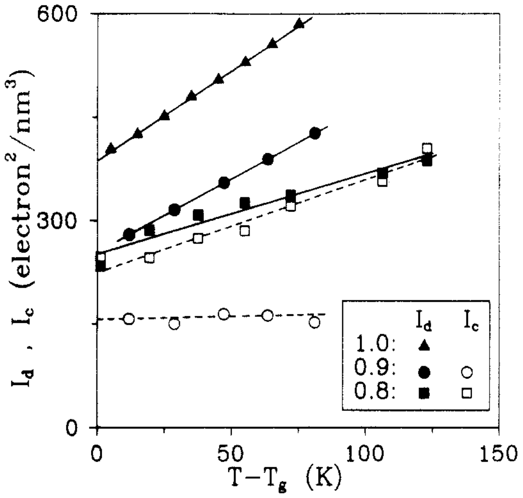

**Figure 6.** Intensities due to density ($I_d$) and concentration ($I_c$) fluctuations in the PCHMA/DOP mixtures as a function of $T - T_g$.

of $T - T_g$. There are two pertinent features in Figure 5. First, the total fluctuations (density and concentration) in the mixtures are identical and nearly equal to the density fluctuations in the bulk polymer. This is a composite effect owing to the suppression of density fluctuations, as inferred from the measured compressibilities (eq 2), and the increase of concentration fluctuations with added plasticizer. Second, there is a mismatch between the measured density fluctuations from SAXS and the ones calculated from the PVT measurements (eq 2) for the bulk polymer, even at $T > T_g$. The difference is about 10% at $T_g$ and we witnessed a similar effect in other poly($n$-alkyl methacrylates) in contrast to the expected behavior (eq 2). This surprising effect will be the subject of a separate study.[18]

The contribution of concentration fluctuations (or of the corresponding intensities, $I_c$) can now be evaluated by subtracting the calculated level of density fluctuations (or $I_d$) from the total fluctuations measured by SAXS. We chose to show this effect for the intensities ($I_d$ and $I_c$), rather than for the fluctuations since we will compare with the corresponding intensities from dynamic light scattering. This is shown in Figure 6 as a function of $T - T_g$. A pertinent feature of Figure 6 is that the density fluctuations become increasingly important with increasing polymer concentration and that their contribution is $T$-dependent. For the PCHMA/DOP (90/10) sample $I_d$ is greater than $I_c$, the former being $T$-dependent whereas for the (80/20) sample $I_d$ and $I_c$ are equal in magnitude and $T$-dependent. The expectation is, that, with increasing plasticizer concentration the contribution of concentration fluctuations will increase and supersede the density fluctuations.

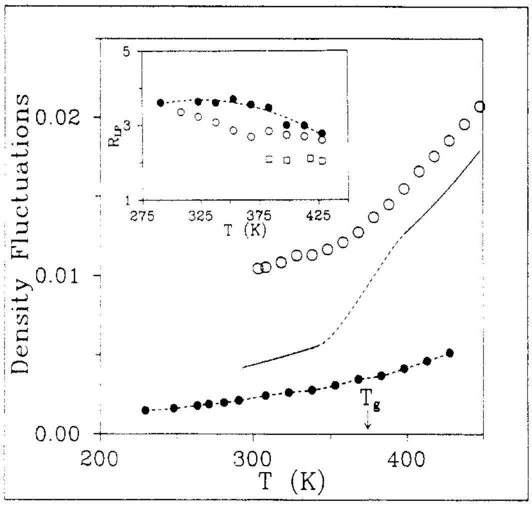

**Figure 7.** Density fluctuations of PCHMA measured by SAXS (○). The solid line gives the calculated density fluctuations (eq 2) from the measured compressibilities. Filled symbols (●) denote the propagating density fluctuations calculated from the Brillouin shift (eq 4). The inset gives the three Landau–Placzek ratios $R_{LP}$: (●) measured from Rayleigh–Brillouin, (○) calculated from SAXS and light scattering, and (□) calculated from PVT and light-scattering data.

It is interesting, at this point, to compare the intensities $I_d$ and $I_c$ obtained from SAXS with the corresponding intensities associated with the dynamics of the density and concentration fluctuations obtained in the light-scattering experiment (photon correlation spectroscopy, PCS), on the same samples (ref 15). Polarized PCS revealed two relaxation processes above $T_g$, as compared to the segmental relaxation in the bulk polymer. The two processes had different dynamics and different intensities. The latter were extracted from the amplitude of the corresponding correlation functions (Figure 7 of ref 15). From the light-scattering data it was concluded that increasing plasticizer concentration has an opposite effect on the intensity arising from density and concentration fluctuations. Namely, $I_d$ decreased whereas $I_c$ was found to increase with plasticizer concentration over the temperature range 338–398 K. Furthermore, at 20% plasticizer concentration, the two intensities were of comparable magnitude. Both findings are in agreement with the SAXS data (Figure 6), notwithstanding the different $Q$-range. SAXS studies have the added advantage of evaluating the intensities to much higher $T$ than $T_g$ which is not possible from the dynamic studies since the process under investigation rapidly shifts out of the correlator window.

The results presented above for the contribution of density and concentration fluctuations can have some consequences in mixed systems. They suggest that incompressibility can only be used as an approximation and certainly fails in concentrated systems. It is expected, that, in mixed systems such as polymer blends, block copolymers, etc., density fluctuations can play an important role. The contribution of density and concentration fluctuations in such systems can be evaluated as outlined above. This work, for block copolymers, is in progress in our laboratory and it is expected to provide new insights into the contribution of density and composition fluctuations.[19]

In the following, we evaluate the contribution of propagating and static components in the measured total fluctuations for the bulk and plasticized polymer. The result for the bulk polymer is shown in Figure 7. The three sets of data correspond to (i) the measured density fluctuations from SAXS (eq 3), (ii) the calculated density fluctuations from the measured isothermal compressibility (eq 2), and (iii) the calculated propagating part of the density fluctuations (phonon contribution) from the measured adiabatic compressibility (eq 4). There are some intriguing features with respect to Figure 7. The propagating density fluctuations are small at $T < T_g$ but increase with $T$. At $T_g$, their contribution is ~25% of the total density fluctuations and at higher $T$ ($\omega\tau \ll 1$) should approach asymptotically $\Psi_S$.[18] Clearly, $\Psi_S$ shows no discontinuity at $T_g$, the only discontinuity appearing in $\beta_T$. The SAXS density fluctuations show only a change in slope at $T_g$, as discussed earlier, and the high values of density fluctuations below $T_g$ is due to "static", frozen-in components during glass formation. From the three sets of data we can define the corresponding $R_{LP}$ (= $\Psi_T/\Psi_S - 1$). With $R_{LP}{}^{SAXS}$, we denote the Landau–Placzek ratio calculated from SAXS, using the measured values of $\Psi_T(T)$ and $\Psi_S(T)$ ($\Psi_S(T)$ is obtained solely from the Rayleigh–Brillouin experiment). $R_{LP}{}^{PVT}$ denotes the same ratio which is now calculated from the $\Psi_T(T)$, obtained from PVT and $\Psi_S(T)$, and $R_{LP}{}^{LS}$ is the measured ratio in the light-scattering experiment. The three ratios are shown in the inset as a function of $T$. Notice that the following double inequality holds:

$$R_{LP}^{LS} > R_{LP}^{SAXS} > R_{LP}^{PVT} \tag{13}$$

The second inequality is due to the excess density fluctuations in the SAXS $Q$-range, discussed earlier. The first inequality points to the existence of excess intensities in the LS $Q$-range (see also Figure 1), notwithstanding $R_{LP}{}^{LS}$ is small in comparison to other bulk polymers. Both inequalities are at variance from eq 2 which predicts only one $R_{LP}$; the lowest ($R_{LP}{}^{PVT}$). Higher $R_{LP}{}^{LS}$ as compared to $R_{LP}{}^{SAXS}$ or $R_{LP}{}^{PVT}$ at temperatures well above $T_g$ have also been observed in glass-forming liquids.[18,20,21] They are thought to be the result of long-range density fluctuations which give rise to excess intensities in the LS $Q$-range. These long-range density fluctuations are observed both in static and dynamic experiments. From the strongly $Q$-dependent intensities in the static light-scattering experiment a correlation length in the range 20–200 nm was obtained. In the dynamic studies they show up as a diffusional mode with relaxation times much longer than the $\alpha$-relaxation times at any temperature.

Figure 8 gives the fluctuations for the plasticized polymer in a similar manner as in Figure 7. The three sets of data correspond to the ones discussed above with respect to the bulk polymer (Figure 7), the only difference being that the SAXS fluctuations are now composed of density and concentration fluctuations. The calculated $R_{LP}$ ratios are also shown in the inset. The same inequality (eq 13) which was discussed for the bulk polymer holds for the mixtures. The second inequality follows here naturally from the presence of concentration fluctuations whereas $R_{LP}{}^{LS} \gg R_{LP}{}^{SAXS}$ at $T < T_g$, indicating excess intensities in the LS $Q$-range.

## Conclusions

In this study we have addressed two issues: (i) how density and concentration fluctuations can be separated in a mixed system and (ii) what is the phonon contribution to the total density fluctuations below and above $T_g$. With respect to the first issue, we found that the separation of the two types of fluctuations is possible with SAXS and $PVT$. In particular, we found that (i) the total fluctuations in the system remain constant and (ii) the density fluctuations are suppressed whereas the concentration fluctuations are enhanced with plasticizer content. As a result, the contribution of density fluctuations cannot be ignored in mixed systems, especially at low plasticizer concentrations. With respect to the second issue, we found that the propagating density fluctuations amount to ~25% of the density fluctuations at $T \approx T_g$ and their contribution increases with $T$, without displaying any discontinuity. The excess intensities observed in the LS and SAXS $Q$-ranges result in the definition of additional Landau–Placzek ratios. These excess intensities and Landau–Placzek ratios are not predicted by conventional liquid-state theories.

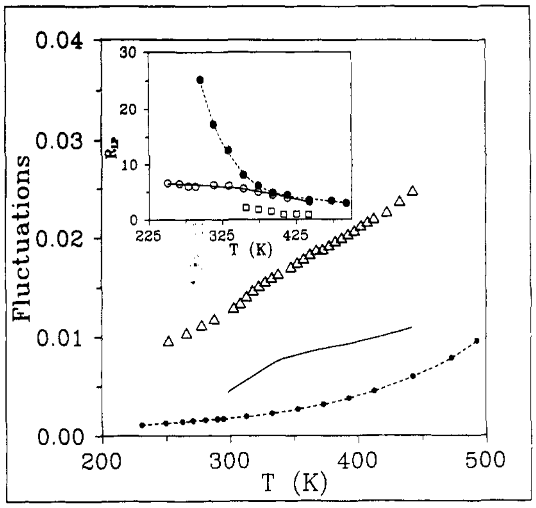

**Figure 8.** Total fluctuations of PCHMA plasticized with 20% DOP and measured by SAXS (△). Solid and dashed lines give the calculated density fluctuations from the measured compressibility and phonon contribution, respectively. The symbols in the inset are the same as in the inset of Figure 7.

**Acknowledgment.** We thank Prof. A. Patkowski for helpful suggestions. Financial support by the German Science Foundation (Sonderforschungsbereich 262) is highly appreciated.

## References and Notes

(1) Wendorff, J. H.; Fischer, E. W. *Kolloid Z. Z. Polym.* **1973**, *251*, 876.
(2) Ruland, W. *Progr. Colloid Polym. Sci.* **1975**, *57*, 192.
(3) Rathje, J.; Ruland, W. *Colloid Polym. Sci.* **1976**, *254*, 358.
(4) Roe, R.-J.; Song, H.-H. *Macromolecules* **1985**, *18*, 1603.
(5) Roe, R.-J.; Curro, J. J. *Macromolecules* **1983**, *16*, 428.
(6) Wiegand, W.; Ruland, W. *Progr. Colloid Polym. Sci.* **1978**, *64*, 147.
(7) Wiegand, W.; Ruland, W. *Colloid Polym. Sci.* **1979**, *257*, 449.
(8) Floudas, G.; Pakula, T.; Stamm, M.; Fischer, E. W. *Macromolecules* **1993**, *26*, 1671.
(9) Guinier, A. *X-Ray Diffraction*; W. H. Freeman and Co.: New York, 1963.
(10) The total density fluctuations measured by SAXS are averages over the frequency spectra of the fluctuations, and a detailed comparison with the propagating density fluctuations requires the spherical average of eq 4 and therefore the frequency dependence of the adiabatic compressibility.
(11) Davidson, N. *Statistical Mechanics*; McGraw-Hill: New York, 1962.
(12) Fischer, E. W.; Hellmann, G. P.; Spiess, H. W.; Hörth, F. J.; Ecarius, U.; Wehrle, M. *Makromol. Chem., Suppl.* **1985**, *12*, 189.

(13) See for example: Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: New York, 1986; Chapt. 5.

(14) Koberstein, J. T.; Picot, C.; Benoit, H. *Polymer* **1985**, *26*, 673.

(15) Fytas, G.; Floudas, G.; Ngai, K. L. *Macromolecules* **1990**, *23*, 1104.

(16) Strobl, G. R. *Acta Crystallogr.* **1970**, *426*, 367.

(17) Olabisi, O.; Simha, R. *Macromolecules* **1975**, *8*, 206.

(18) Floudas, G.; Fischer, E. W.; Pakula, T. Manuscript in preparation.

(19) Floudas, G.; Vogt, S.; Pakula, T.; Fischer, E. W. *Macromolecules* **1993**, *26*, 7210.

(20) Fischer, E. W.; Becker, Ch.; Hagenah, J.-U.; Meier, G. *Progr. Colloid Polym. Sci.* **1989**, *80*, 198.

(21) Fischer, E. W.; Meier, G.; Rabenau, J.; Patkowski, A.; Steffen, W.; Thönnes, W. *J. Non-Cryst. Solids* **1991**, 131–133, 134.