# Quasielastic gamma-ray scattering from polydimethylsiloxane in benzene solutions

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Quasielastic gamma-ray scattering of 46.5-keV Mössbauer photons by polydimethylsiloxane has been studied at room temperature as a function of dilution in benzene. The high energy resolution of this novel technique allowed the separation of the scattering signal into a narrow component associated with stiff motions along the polymer chain backbone and a quasielastic component associated with softer side group motions. The narrow component disappears upon dilution in benzene while the intensity of the quasielastic component grows proportionately. This result is interpreted as a softening of the backbone normal modes upon dilution.

## INTRODUCTION

A newly developed technique[1] using quasielastic gamma-ray scattering (QEGS) has been used for the first time to investigate the dynamics of macromolecular liquids. The $\mu$eV energy resolution provided by this technique opens up new possibilities for the study of molecular liquids in general and macromolecular liquids in particular.

Figure 1 summarizes the main techniques used to investigate the dynamics of liquids[2-4] at various characteristic length scales going from the collision dominated hydrodynamic region (very small $Q$ and $\omega$) to the free streaming ideal gas limit (very large $Q$ and $\omega$). Here, $\hbar Q$ and $\hbar\omega$ represent the momentum and energy transferred during scattering. Typical characteristic lengths (Angstroms) and time scales (picoseconds) for liquids fall within the $(Q,\omega)$ windows for neutron scattering, gamma-ray scattering and computer simulation (molecular and Brownian dynamics). While many attempts have been made to use Fe-57 Mössbauer gamma-ray sources for this type of study, the maximum photon intensities available are so low as to severely limit their utility. Using high intensity Ta-183 sources with the QEGS facility has opened the door for photon scattering studies over a large $Q$ range with $\mu$eV energy resolution.

The scattering of gamma rays is a pure coherent process (in momentum space) so that the QEGS technique measures the coherent quasielastic dynamic structure factor. Cold neutrons have also been very useful for quasielastic scattering since very high energy resolutions can be achieved with several techniques[5] (time-of-flight, backscattering, neutron spin-echo spectrometers). However, normal (i.e., nondeuterated, sometimes referred to as hydrogenated) molecular liquids scatter neutrons mostly incoherently, while deuterated molecular liquids are characterized by a mixture of coherent and incoherent neutron scattering so that the coherent scattering signal can be obtained only indirectly.

In solids, normal modes are characterized by correlation times $t_c$, which are very much slower than the scattering times $t_i$ (interaction time between photons and atoms). For highly viscous molecular liquids, however, there is a wide range of $t_c$'s such that modes with $t_c = t_i$ can be found. Note that some solids (especially "soft" solids such as bulk hydrocarbons) can also sustain a wide range of normal modes, including quasielastic modes.[6,7]

Macromolecular liquids sustain a wide spectrum of normal modes going from very stiff ones describing the dynamics of rigid bond lengths and angles (such as those along the polymer chain backbone) to very soft ones describing the dynamics of dangling side groups and chain ends. The purpose of the present investigations was to observe the "softening" of the rigid modes upon dilution of the macromolecules in a good solvent. Polydimethylsiloxane (PDMS) was chosen because it is a melt at room temperature and contains Si atoms which are relatively good gamma-ray scatterers. The QEGS technique was used to quantify the relative contributions of such modes; the stiff ones contributed energy widths narrower than the instrumental width (8 $\mu$eV), while the soft ones were resolved by our QEGS instrument and are

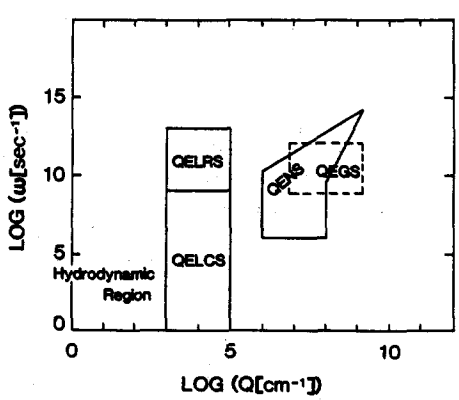


FIG. 1. Diagnostic methods used to investigate the dynamics of liquids: quasielastic light Rayleigh scattering (QELRS), quasielastic light correlation spectroscopy (QELCS), quasielastic neutron scattering (QENS), and quasielastic gamma-ray scattering (QEGS). The computer simulation region (molecular or Brownian dynamics) overlaps with QENS and QEGS.

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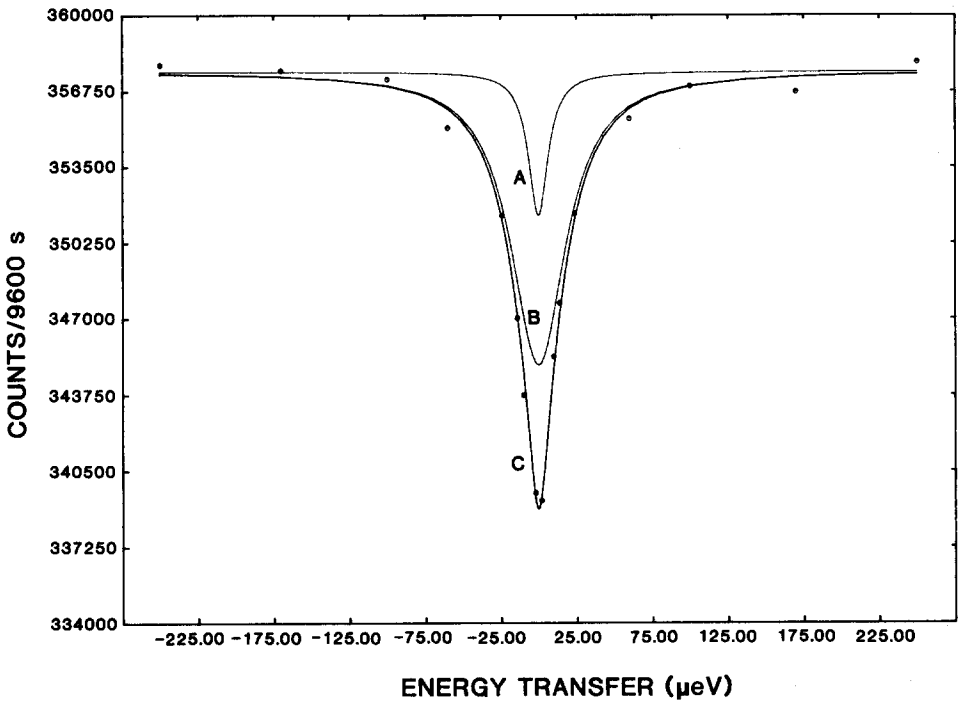


FIG 2. QEGS spectrum from undiluted polydimethylsiloxane taken at room temperature with $Q = 0.9\text{Å}^{-1}$. Curves $A$ and $B$ give the individual Lorentzian fits for the narrow width and quasielastic scattering components, respectively. Curve $C$ gives the overall fit to the data points indicated by circles.

referred to as quasielastic.

A recent experiment performed with the QEGS instrument investigated the temperature and scattering angle dependences of the quasielastic width in liquid pentadecane.[8] In that study, the QEGS width was seen to increase with temperature and to narrow at the maximum of the structure factor (de Gennes narrowing).

## EXPERIMENT

The QEGS instrument has been described elsewhere[1] in detail. It uses intense Mössbauer sources (Ta-183, $T_{1/2} = 5.1$ day) cooled to liquid nitrogen temperature. These sources yield intensities approximately 1000 times higher than conventional Fe-57 Mössbauer sources. The incident photons of 0.267 Å wavelength which are quasielastically scattered in the sample are resonantly absorbed by Doppler shifting the absorber. The shifting is achieved by having the beam pass (twice) through a circumferential natural $W$ foil, 25 microns thick, mounted on a rotor with 15 cm radius. The rotor is driven at velocities corresponding to energy shifts of 1 to 500 $\mu$eV. The photons that are not absorbed are counted by an intrinsic germanium detector. The resolution of the detector allows separation of the Mössbauer gamma rays from other photons present in the source spectrum. Despite the strong sources, however, counting times are still of the order of days because incident and scattered beams are limited by 3 mm $\times$ 2.5cm $\times$ 20cm and 6mm $\times$ 2.5cm $\times$ 11cm collimators before and after the sample, respectively. The source-sample and sample-detector distances are both approximately 75 cm.

Liquid samples were placed in a cell with 50 $\mu$m thick Kapton windows (to minimize background scattering) which had a sample thickness of 3.3 cm corresponding to 50% transmission. A polydimethylsiloxane (PDMS) melt of molecular weight ($M_w = 77\,000$ and $M_n = 31\,000$) was purchased form Aldrich Chemical. QEGS data were recorded for this PDMS sample (see Fig. 2) and other PDMS/Benzene solutions at various concentrations (see

TABLE I. QEGS from polydimethylsiloxane/benzene solutions. In the two-Lorentzian fit, the width of the first Lorentzian was fixed equal to the instrumental width of 8 $\mu$eV. Data were taken at room temperature with $Q = 0.9\ \text{Å}^{-1}$. Numbers in parentheses are uncertainties.

| Benzene/PDMS concentration by weight (%/%) | Counting time (h) | Two-Lorentzian fit $A_1/B$ (%) | $A_2/B$ (%) | $\Gamma_2$ ($\mu$eV) |
|---|---|---|---|---|
| 0/100 | 48 | 2.03(0.13) | 4.19(0.08) | 22.8(1.0) |
| 17/83 | 84 | 1.24(0.12) | 3.03(0.08) | 33.5(2.3) |
| 40/60 | 120 | 0.16(0.12) | 2.07(0.06) | 52.9(4.5) |
| 60/40 | 120 | 0.01(0.15) | 1.39(0.08) | 77.1(11.5) |
| 100/0[a] | 144 | 0.0 | 0.0 | Too broad to be observed |

[a] This entry represents pure benzene where no Mössbauer signal was observed.

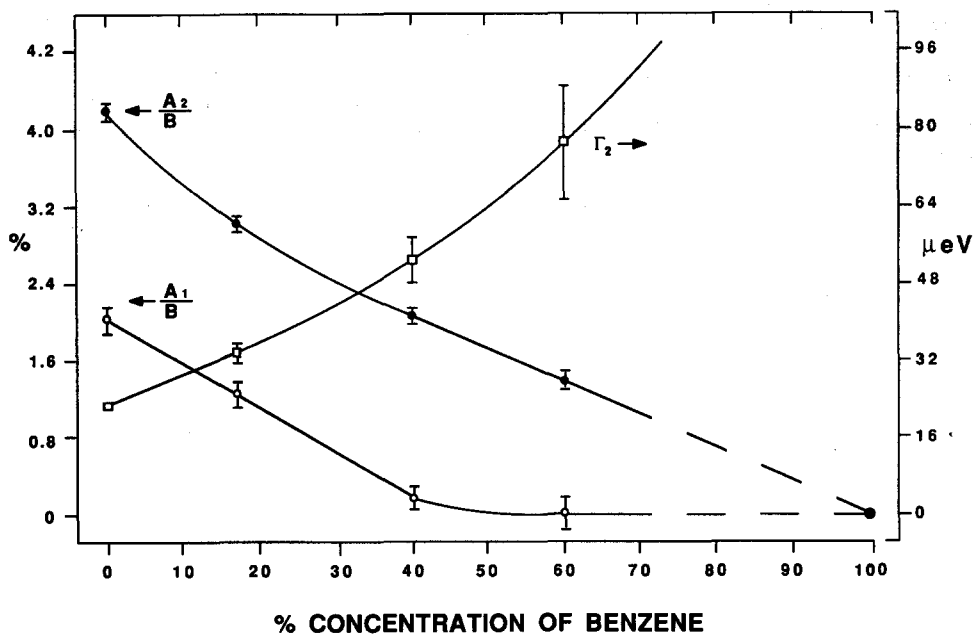


FIG 3. The scale on the left of the figure gives the relative amplitudes $A_1/B$ and $A_2/B$ in % for the narrow width and quasielastic scattering components, respectively, versus the concentration of benzene. The scale on the right gives the width $\Gamma_2$ in $\mu$eV for the quasielastic component. No Mössbauer signal was observed for the 100% benzene sample. All data were taken at room temperature with the scattering angle set to the first peak of the structure factor $Q = 0.9\text{Å}^{-1}$. The solid lines are included as a guide to the eye.

Table I) at room temperature with the scattering angle set to correspond to the first peak ($Q = 0.9\ \text{Å}^{-1}$) of the structure factor $S(Q)$.

## DATA TREATMENT AND DISCUSSION

Since the goal of these investigations was to observe general features, a simple data treatment scheme was used which consisted of fitting the QEGS signal, $I(Q,\omega)$, to a sum of two Lorentzians:

$$I(Q,\omega) = B - S(Q,\omega),$$

where

$$S(Q,\omega) = A_1(\Gamma_1/2)/[\omega^2 + (\Gamma_1/2)^2] + A_2(\Gamma_2/2)/[\omega^2 + (\Gamma_2/2)^2].$$

$B$ represents the continuum from which the resonant scattering signal is subtracted and $S(Q,\omega)$ is the dynamic structure factor. $A_1$ and $A_2$ are the amplitudes of the narrow and quasielastic Lorentzian components. The first Lorentzian (with a full width at half maximum $\Gamma_1$) describes the narrow width scattering component arising from the stiff modes while the other Lorentzian (of FWHM $\Gamma_2$) corresponds to the quasielastic contribution from the soft modes. $\Gamma_1$ was fixed equal to the instrumental width for elastic scattering from a LiF crystal[1] of 8 $\mu$eV. The width of the second Lorentzian reduces to $\Gamma_1$ for solid state samples.

Table I summarizes the quasielastic widths $\Gamma_2$ and the signal-to-continuum ratios $A_1/B$ and $A_2/B$ obtained from using a nonlinear least-squares-fitting procedure. The $A_1/B$ and $A_2/B$ ratios are plotted in Fig. 3 along with $\Gamma_2$. Since the QEGS data were taken in constant-$Q$ scans, no explicit $Q$ dependence was considered for $A_{1,2}$ and $\Gamma_{1,2}$.

Three important observations can be made: (1) The quasielastic width $\Gamma_2$ increases for increasing dilution. (2) The narrow width scattering component $A_1/B$ decreases to zero at about 40% dilution. (3) While the $A_2/B$ ratio also decreases with increasing dilution, the overall quasielastic intensity, as measured by the $(A_2/B)/\Gamma_2$ product, increases by 12% as the intensity of the narrow component is transferred into the quasielastic component. With 100% benzene in the sample cell, no Mössbauer signal was observed as noted in Table I. Within the QEGS instrument energy width of 8 $\mu$eV, the percentage of stiff to soft modes at room temperature and no benzene dilution was determined from $(A_1\Gamma_1/B)/(A_2\Gamma_2/B)$ to be 17%.

In conclusion, this short contribution reports on the application of a novel technique (QEGS) to observe the dynamics of PDMS in benzene solutions. Qualitative observation of the disappearance of the narrow width scattering component upon dilution has been interpreted as a softening of stiff degrees of freedom along the chain backbone. A more precise understanding of these normal modes (which ones are dominant and how they vary) that contribute to the QEGS signal, however, could be better understood in conjunction with molecular dynamics computer simulations. When supplemented by such a modeling backup, the QEGS technique could prove valuable in the understanding of the dynamics of a number of macromolecular systems such as the effect of bulky side groups and of branching in polymer solutions, as well as the freezing-in of the various degrees of freedom in liquid crystals.

## ACKNOWLEDGMENTS

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