# Neutron Scattering from Star Polymers in a Matrix of Homopolymers

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ABSTRACT: The neutron-scattering experiments performed by Ewen[1] et. al. are reinterpreted by means of random phase approximation (RPA). The Gaussian chain model and Rouse dynamics are utilized to obtain the bare system form factors and mobilities of a star polymer and matrix homopolymer. It is demonstrated that how the static and dynamic scattering experiments can be combined to obtain the statistical segment length and corresponding friction coefficient as well as the radius of gyration of the arms of a star polymer in the matrix of a homopolymer via RPA.

## 1. Introduction

The purpose of this short communication is to reinterpret the elastic and quasi-elastic neutron-scattering experiments reported by Ewen[1] et al. investigating the segmental conformations of, and relaxation in, star polymers in a melt of linear macromolecules. The neutron-scattering experiments were performed at ILL Grenoble (France) using D17 for the elastic and the neutron spin echo spectrometer IN11 for the quasi-elastic measurements. In the experiment, a 12-arm star of alternating poly(ethylene−propylene) (PEP) copolymer arms ($M_w = 60\ 000$ g/mol, $M_w/M_n = 1.02$) is blended with a corresponding low molecular weight deuterated copolymer ($M_w = 5.000$ g/mol, $M_w/M_n = 1.02$). The concentration of the star polymer was 10%. Further details of the experiment are given elsewhere.[1] Since the Flory interaction parameter between the monomers belonging to the star polymers and homopolymers is zero, if deuteration is assumed not to effect the chemical properties of the monomers, the mixture can be regarded as one with two noninteracting components in the general theory of interacting multicomponent polymer mixtures.[2,3]

## 2. Description of the Theory

**2.1. Statics.** In the framework of the random phase approximation (RPA), the static structure factors of polymers in an interacting system are given in terms of the bare system static structure factors. When we consider star polymers in a matrix of homopolymers, the static structure factor of the star polymer in the interacting system is given as[2−5]

$$\frac{1}{S_{ss}(q)} = \frac{1}{S^0_{ss}(q)} + \frac{1}{S^0_{hh}(q)} \tag{1}$$

where $S^0_{ss}(q)$ is the static structure factor of a star polymer in the bare system and can be written as

$$S^0_{ss}(q) = \phi_s p_s P_{ss}(p,f_s,\alpha) \tag{2}$$

where $\phi_s$ is the ratio of the number of segments in the star polymer to the total number of segments in the mixture, $p_s$ is the number of segments in the star polymer molecule, $p$ is the number of segments in one arm of the star polymer molecule, $f_s$ is the functionality of the star polymer molecule, so that $p_s = f_s p$ and $\alpha = q^2a^2/6$ where $a$ is the statistical segment length and $q$ is the wavenumber. The $P_{ss}(p,f_s,\alpha)$ in eq 2 denotes the form factor of a star polymer molecule, and given by[3]

$$P_{ss}(p,f_s,\alpha) = \frac{1}{f_s}\{P_{11}(p,\alpha) + (f_s - 1)P_{12}(p,\alpha)\} \tag{3}$$

where $P_{11}(p,\alpha)$ denotes the static structure factor of one arm of the star polymer molecule, i.e., of a linear Gaussian chain containing $p$ segments, and $P_{12}(p,\alpha)$ is the partial structure factor between two arms of a star polymer molecule. The static structure factor of the matrix in the bare system denoted by $S^0_{hh}(q)$ in eq 2 is given by

$$S^0_{hh}(q) = (1 - \phi_s)pP_{11}(p,\alpha) \tag{4}$$

where $P_{11}(p,\alpha)$ denotes the form factor of the matrix homopolymer. It is the same as the form factor of an arm of a star polymer appearing in eq 3 because in this experiment the matrix homopolymers and the arms of the stars are identical in all respects except for their scattering lengths. Indeed, when $f_s = 1$, eqs 2 and 4 become identical except for their volume fractions.

The full expression of $P_{11}(p,\alpha)$ for a linear Gaussian chain with a statistical segment length $a$ and number of statistical segments $p$ is given[5] by

$$P_{11}(p,\alpha) = \frac{1}{p}\left\{1 + 2\frac{e^{-\alpha}}{(1 - e^{-\alpha})}\left[1 - \frac{1 - e^{-p\alpha}}{p(1 - e^{-\alpha})}\right]\right\} \tag{5}$$

which, in the limit of $a \to 0$ and $p \to \infty$, keeping $pa^2$ constant, reduces to the well-known Debye function:[7]

$$P_D(x) = \frac{2}{x^2}[x - 1 + e^{-x}] \tag{6}$$

where $x = q^2R_g^2$ and $R_g^2 = pa^2/6$ is the radius of gyration of an arm, or of a matrix homopolymer. The Debye form and the full expression $P_{11}$ coincide with each other when $qa \ll 1$ and differ for large values of $q$. The former

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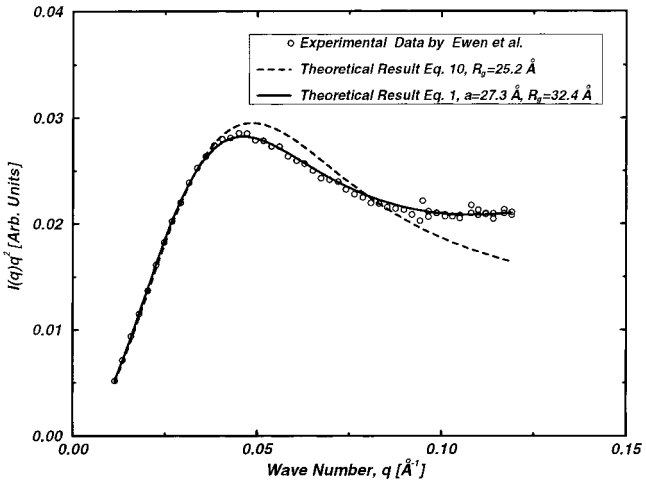


**Figure 1.** Variation of the scattering intensity as a function of wavenumber for a 12-arm alternating PEP star polymer in a melt of corresponding linear chains.

vanishes as $2/x$ as $q \rightarrow \infty$, whereas the full expression approaches $1/p$. Since the spin echo scattering experiments usually explore the large $q$ region of $qa \approx 1$, and the segmental motions are important, the full expression of the single-chain form factor is needed in the interpretation of data.

The same comments are also applicable to the partial form factor $P_{12}(p,\alpha)$ between two arms of the star polymer in eq 3. When the arms are identical, this has been calculated as[8]

$$P_{12}(p,\alpha) = \frac{e^{-\alpha}}{p^2}\frac{(1 - e^{-p\alpha})^2}{(1 - e^{-\alpha})^2} \tag{7}$$

which reduces, when $qa \ll 1$, to the known result[9]

$$P_{12}(x) = \frac{(1 - e^{-x})^2}{x^2} \tag{8}$$

The form factor $P_{ss}(q)$ of a star polymer in eq 3 reduces to the well-known result due to Benoit,[10] when $qa \ll 1$,

$$P_{ss}(x) = \frac{2}{f_s x^2}\left(x - 1 + e^{-x} + \frac{(f_s - 1)}{2}(1 - e^{-x})^2\right) \tag{9}$$

where, as before, $x = q^2R_g^2$. This result is obtained by substituting eqs 6 and 8 into eq 3. In the interpretation of the elastic scattering data Ewen et al. used eq 1 without the second term, and eq 9 in

$$S_{ss}(q,x) = \phi_s p_s P_{ss}(q,x) \tag{10}$$

which does not contain information on the segments length. Thus the only unknown is the radius of gyration of an arm of the star polymer appearing in $P_{ss}(q)$. Since the scattering intensity is measured in arbitrary units, one has also to introduce a scaling factor in front of eq 10, which is related to the scattering lengths and the experimental parameters. Following the interpretation of Ewen and his co-workers, we obtained a radius of gyration of the arm of the star polymer $R_g = 25.2$ Å by using a nonlinear curve-fitting technique. The results of the elastic scattering experiment on the PEP star system in the presence of the low molecular weight PEP chains are compared with the theoretical prediction dashed curve, on the basis of eq 10 in Figure 1. Although the agreement is very satisfactory in the small $q$ region, the analytical curve deviates appreciably from the experimental data on the high $q$ region. Ewen et al. attributed these deviations to the arm conformations and argued that the arms are more correlated than the predictions of the Gaussian chain model.

We now interpret the same data given by Ewen et al. using the results of RPA, i.e., eq 1, without ignoring the presence of the matrix and using the full expression of the form factors given by eqs 5 and 7. Since matrix homopolymers and the arms of the star polymers have the same statistical properties, the unknown parameters in this case are statistical segment length, radius of gyration, or number of segments in one of the arms of the star polymer molecule and the scaling constant. We obtained the radius of gyration of an arm $R_g = 32.4$ Å and the statistical segment length $a = 27.3$ Å. The resulting curve is given in Figure 1 as a solid line, and it is observed that the agreement between experimental data and theoretical results is significantly improved in the high $q$ region.

The present interpretation differs from the one reported by Ewen[1] et al. in which eq 10 is used with the Debye expression of the form factor of the star polymer given by a dashed line in Figure 1. Besides yielding a value for the statistical segment length, moreover, the present interpretation also enables one to obtain a relationship between the apparent radius of gyration for the binary mixture of star polymers in the matrix of identical homopolymers and the radius of gyration of a star polymer. The former is defined by representing $S_{ss}(q)$ in eq 1 as

$$S_{ss}(q) = S_{ss}(q = 0)\left(1 - \frac{q^2 R_{gapp}^2}{3}\right) \tag{11}$$

for $q^2R_g^2 \ll 1$, and evaluating $S_{ss}^0(q)$ and $S_{hh}^0(q)$ also in the small $q$ limit using the Debye expression for the form factors in this limiting case. Finally one obtains

$$R_{gapp}^2 = \frac{(1 - \phi_s)(3f_s - 2)/f_s + \phi_s f_s}{1 + (f_s - 1)\phi_s} R_g^2 \tag{12}$$

The radius of gyration of a star polymer, on the other hand, is obtained from $S_{ss}^0(q)$ by the same procedure as

$$R_{gs}^2 = \frac{(3f_s - 2)}{f_s} R_g^2 \tag{13}$$

which, of course, also follows from eq 12 with $\phi_s \rightarrow 0$. Using $R_g = 32.4$ Å, $f_s = 12$ and $\phi_s = 0.1$, we find $R_{gapp} = 43.3$ Å and $R_{gs} = 54.5$ Å, which shows that $R_{gapp} \leq R_{gs}$ when the star polymers embedded in a homopolymer matrix which has the same radius of gyration as the arm of the star polymer molecule.

If one interprets the data in Figure 1 using eq 10, the curve fitting yields the radius of gyration of a single arm as $R_g = 25.2$ Å and the radius of gyration of the star polymer as $R_{gs} = 42.4$ Å which is the apparent radius of gyration of the polymer blend and the resulting radius of gyration of the star polymer becomes incorrect.

**2.2. Dynamics without Hydrodynamic Interactions.** In an incompressible binary polymer blend of star polymers in a matrix of homopolymers, the short time behavior of the dynamic scattering function of star polymers $S_{ss}(q,t)$ is given by

$$S_{ss}(q,t) = e^{-\Omega_{ss}(q)t} S_{ss}(q) \tag{14}$$

where $S_{ss}(q)$ is the static structure factor of star polymers in the interacting system, which is given by eq 1 and $\Omega_{ss}(q)$ is the first cumulant. The latter is related to the short time mobility of the star polymer in the interacting system $m_{ss}(q)$ and the interacting system static structure factor $S_{ss}(q)$ of the star polymer as follows:

$$\Omega_{ss}(q) = q^2 k_B T \frac{m_{ss}(q)}{S_{ss}(q)} \tag{15}$$

where $m_{ss}(q)$ is expressed in terms of the bare system mobilities according to the by inverse superposition rule:[2,4,11,12]

$$\frac{1}{m_{ss}(q)} = \frac{1}{m^0_{ss}(q)} + \frac{1}{m^0_{hh}(q)} \tag{16}$$

The bare system mobilities are calculated using the Rouse dynamics as

$$\frac{1}{m^0_{ss}(q)} = \frac{\phi_s}{\zeta} \tag{17}$$

$$\frac{1}{m^0_{hh}(q)} = \frac{(1-\phi_s)}{\zeta} \tag{18}$$

where $\zeta$ is the friction coefficient per segment. Using eqs 17 and 18 into eq 16, we obtain the short time mobility $m_{ss}(q)$ in the interacting system as

$$m_{ss}(q) = \frac{\phi_s(1-\phi_s)}{\zeta} \tag{19}$$

The first cumulant is then obtained from eqs 1 and 15 as

$$\Omega_{ss}(q) = q^2 k_B T \frac{\phi_s(1-\phi_s)}{\zeta}\left[\frac{1}{S^0_{ss}(q)} + \frac{1}{S^0_{hh}(q)}\right] \tag{20}$$

In eq 20 we ignored the hydrodynamic interactions and used Rouse dynamics. The first cumulant can also be calculated with hydrodynamic interactions in eq 15 by using the preaveraged Oseen tensor.

We wish to interpret the experimental data for $\Omega_{ss}(q)$ obtained with neutron spin echo spectroscopy by Ewen and his co-workers using eq 20. The unknown parameters in eq 20 are the friction coefficient $\zeta$, segment length "$a$", and the radius of gyration of an arm of star polymers. First, we use the radius of gyration $R_g = 32.4$ Å and $a = 27.3$ Å, which are obtained from elastic scattering data. The resulting analytical curve (dashed line) is compared with the experimental data in Figure 2. Since the neutron spin echo explores the higher $q$ region than that in the elastic scattering experiments, and therefore more sensitive to the segmental length, we reinterpreted the same data for $\Omega_{ss}(q)$ by using only the radius of gyration of an arm of the star as a known parameter obtained from elastic scattering data, and by treating the segment length $a$ as unknown parameters in eq 10. This time we obtained the the statistical segment length as $a = 24.5$ Å. The

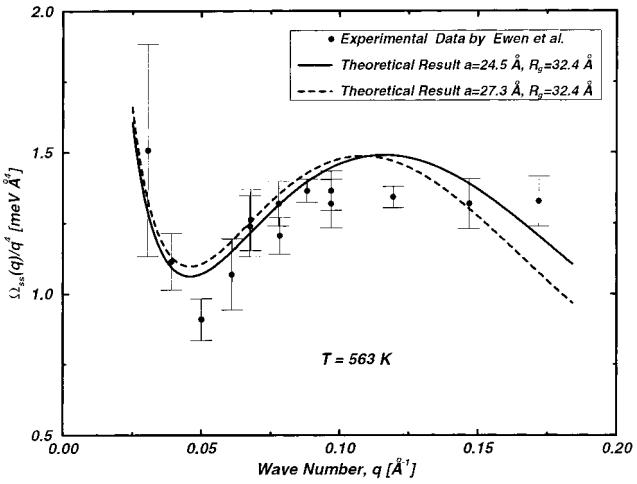


**Figure 2.** Variation of the first cumulant with wavenumber for a 12-arm alternating PEP star polymer in a melt of corresponding linear chains.

agreement between theoretical prediction (solid line) and experimental data is noticeably better, especially in the high $q$ region. We consider the new value of $a =$ 24.5 Å as a better estimate for the statistical segment length.

The above procedure also yields the friction coefficient $\zeta$, because $\Omega_{ss}(q)$ is inversely proportional to it. This however requires accurate absolute values of $\Omega_{ss}(qq)$. We obtain $\zeta_A = 1.247 \times 10^{-8}$ g s$^{-1}$ with the data given by Ewen et al. We conclude from the above data analysis that the spin echo experiments can provide useful information for the statistical segment length $a$ and corresponding friction coefficient $\zeta$, complementing the static scattering experiments that yield the radius of gyration $R_{gA}$.

The combination of static and spin echo dynamic scattering experiments on the same system enables one to determine consistently these parameters, which characterize chains in the spring bead model. We believe that the segment length is an adjustable parameter in the Gaussian chain model, below which the chain can no longer be treated as Gaussian and its value may be different in different experiments. In other words, it is the shortest distance below which the chain stiffness becomes increasingly noticeable. The results of the segment length obtained from static and dynamic scattering data in the Gaussian chain model provide a reasonable fit in the framework of the model and can be treated as the length below which the Gaussian chain model cannot be used.

## References and Notes

(1) Ewen, B.; Richter, D.; Fetters, L. J.; Huang, J. S.; Farago, B. Neutron Scattering Studies on the Relation Between Structure and Dynamics of Star Shaped Polymers. *J. Non-Cryst. Solids* **1991**, *131−133*, 697.

(2) Akcasu, A. Z.; Tombakoglu, M. Dynamics of Copolymer and Homopolymer Mixtures in Bulk and in Solution via Random Phase Approximation. *Macromolecules* **1990**, *23*, 607.

(3) Tombakoglu, M. *Dynamics of Multicomponent Polymer Mixtures*; Ph.D. Thesis, The University of Michigan, Ann Arbor, MI, 1991.

(4) de Gennes, P. G. *Scaling Concept in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(5) Akcasu, A. Z.; Benmouna, M.; Benoit, H. Application of Random Phase Approximation to the Dynamics of Polymer Blends and Copolymers. *Polymer* **1986**, *27*, 1935.

(6) Akcasu, A. Z.; Gurol, H. Quasi-elastic Scattering by Dilute Polymer Solutions. *J. Polym. Sci.* **1976**, *14*, 1.
(7) Debye, P. Molecular Weight Determination by Light Scattering. *J. Phys., Coll. Chem.* **1947**, *51*, 18.
(8) Tombakoglu, M.; Akcasu, A. Z. Interpretation of Dynamic Scattering Experiments on Ternary Polymer Mixtures. *Polymer* **1992**, *33*, 1127.
(9) Benoit, H.; Hadziioannoua, G. Scattering Theory and Properties of Block Copolymers with Various Architectures in the Homogeneous Bulk State. *Macromolecules* **1988**, *21*, 1449.
(10) Benoit, H. On the effect of Branching and Polydispersity on the Angular Distribution of the Light Scattered by Gaussian Coils. *J. Polym. Sci.* **1953**, *17*, 507.
(11) Pincus, P. Dynamics of Fluctuations and Spinodal Decomposition in Polymer Blends. II. *J. Chem. Phys.* **1981**, *75*, 1996.
(12) Binder, K. Collective Diffusion, Nucleation, and Spinodal Decomposition in Polymer Mixtures. *J. Chem. Phys.* **1983**, *79*, 6387.

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