Microscopic Dynamics of Polyethylene Glycol Chains Interacting with Silica Nanoparticles

T. Glomann,[1] G. J. Schneider,[1,*] J. Allgaier,[1] A. Radulescu,[1] W. Lohstroh,[2] B. Farago,[3] and D. Richter[1]

[1]*Jülich Centre for Neutron Science, Forschungszentrum Jülich, 52425 Jülich, Germany
and Outstation at FRM2, 85747 Garching, Germany*
[2]*Heinz Maier-Leibnitz Zentrum, Technische Universität München, Lichtenbergstraße 1, 85747 Garching, Germany*
[3]*Institut Laue-Langevin, 6 rue Jules Horowitz, 38042 Grenoble, France*
(Received 23 December 2012; published 23 April 2013)

We present high resolution neutron spectroscopic investigations of polyethylene glycol matrices interacting attractively with neat SiO_2 nanoparticles. We observe a very rich dynamical picture that significantly contradicts earlier conclusions on such systems. Investigating a short chain matrix we realized that a fraction of chains is attached at the nanoparticle surface suppressing completely its translational diffusion. Nevertheless these attached chains undergo an unchanged segmental dynamics seemingly forming a micellelike corona of chains attached with their OH end groups. Changing to methyl-terminated chains the picture changes drastically, now showing a tightly adsorbed layer that however is not glassy as often assumed but undergoes fast picosecond local dynamics. With the singular importance of end groups, mean field approaches are not applicable and future simulations should be redirected to model such unexpected phenomena.

Chain and surface interactions determine essentially the mechanical, optical, and electrical properties in polymer based nanocomposites. The molecular mechanisms and their chemical ingredients are very complex and remain poorly understood. In a step toward a better understanding of the interplay between chain dynamics and chain surface interactions in particle-filled nanocomposite melts we want to exploit the high spatial and temporal resolution of neutron spectroscopy to illuminate the changes of the polymer dynamics caused by a finite attractive interaction between chains and surfaces.

In general, the mechanical properties of such nanocomposites are discussed in terms of networklike approaches [1,2]. Those models suggest adsorbed chains exhibiting an immobilized shell around the particles with dangling ends, loops, and chains connecting nanoparticles when the wall-to-wall distance becomes comparable to twice the chain end-to-end distance R_{ee} [1–3]. Even at low adsorption energies strong adsorption may occur due to multiple adsorption sites.

For the case of polyethylene glycol (PEG) melts filled with SiO_2 particles, where the chains are either terminated by OH or CH_3 end groups, NMR studies inferred three different phases of mobility for the polymer chains [4]: (i) A glassy layer with about 1 nm thickness that is independent of the matrix molecular weight and does not change with the temperature. (ii) A fraction with intermediate relaxation time to which networklike properties were ascribed and (iii) a bulklike highly mobile fraction. A similar classification of the dynamics was also reported for PDMS based nanocomposites [5]. The NMR experiments also revealed that the different end groups lead to the same dynamical behavior over a large molecular weight

range [4,6]. However, other studies report on the possible influence of end groups on the adsorption characteristics of the PEG backbone even at high molecular weights [7]. Furthermore, extensive structural studies using small-angle x-ray and neutron scattering (SAXS, SANS) were performed and interpreted with mean field calculations based on the polymer reference interaction site model [8]. There, an average interaction energy of $0.5k_BT$ per monomer was found. Furthermore, based on various spectroscopic techniques there seems to be a general agreement about the existence of a ≈ 1 nm thick glassy polymer layer around nanoparticles [9,10].

In this work we present a study on the chain dynamics in model systems of linear PEG filled with SiO_2 nanoparticles from a very local to the global scale. Both, OH- and methyl-end groups were considered. Employing neutron spin echo (NSE) and high resolution time-of-flight (TOF) spectroscopy a very rich dynamical picture evolved that contradicts earlier conclusions on the polymer dynamics in nanocomposites with attractive polymer nanoparticle interaction. (i) PEG-$(OH)_2$ chains graft with their end group on the SiO_2 surface and display the Rouse-like dynamics of end-grafted chains. (ii) CH_3-terminated chains form a confining layer of ≈ 1 nm thickness but with high internal mobility. (iii) Locally, both chains exhibit picosecond dynamics with no signature of a glassy layer, leading in both cases to the same segmental (Rouse) relaxation rate as in the bulk.

On a coarse grained level and at intermediate length scales the segmental dynamics of polymer chains is well described by the Rouse model [11] that treats the dynamics of a Gaussian chain in a heat bath. Entropic forces originating from the conformational chain entropy and

frictional forces from the heat bath drive the dynamics. The model's solution is relaxation modes with relaxation times decreasing with the mode number p^2. All internal modes have fully relaxed after the so-called Rouse time τ_R. The model is governed by one parameter: the monomeric friction coefficient ζ. The dynamic structure factor reads [12]:

$$\frac{S(Q,t)}{S(Q)} = \frac{1}{f_p N} \sum_{i,j}^{N} \exp\left\{-Q^2 D_R t - \frac{Q^2 \ell^2}{6}|i-j| - \frac{2Q^2 R_{ee}^2}{3\pi^2}\right.$$

$$\left. \times \sum_{p=1+p_0}^{N} \frac{f_p}{p^2} \cos\left(\frac{p\pi i}{N}\right)\cos\left(\frac{p\pi j}{N}\right)\left[1-\exp\left(-\frac{p^2 t}{\tau_R}\right)\right]\right\}, \quad (1)$$

where $R_{ee} = N\ell^2$ is the chain end-to-end distance, ℓ the segment length, $W = 3k_B T/(\ell^2 \zeta)$ the Rouse rate, $D_R = W\ell^4/(3R_{ee}^2)$ the Rouse diffusion coefficient and $\tau_R = N^2/(\pi^2 W)$ the Rouse time. Finally f_p and p_0 depend on the boundary conditions ($p_0 = 0$, $f_p = 1$ free chain, $p_0 = -1/2$, $f_p = 1/2$ chain with one end fixed). It is clear from the expressions that the elementary Rouse rate is the only parameter of the Rouse model from which all other dynamic parameters can be deduced. Underlying the segmental Rouse dynamics are fast local picosecond motions around the main chain bonds.

The experiments were performed on monodisperse PEG chains that were anionically synthesized featuring either OH or CH_3 end groups. The average number molecular weights were: h-PEG-$(OH)_2$ 1.8 kg/mol; d-PEG-$(OH)_2$ 1.9 kg/mol; h-PEG-$(CH_3)_2$ 2.2 kg/mol; d-PEG-$(CH_3)_2$ 2.0 kg/mol. Silica nanoparticles without surface modification were obtained from Nissan Chemical (SNOWTEX® ST-40) and characterized by SANS. The charge stabilized nanoparticles have a log normal size distribution with average diameter $\langle D \rangle = 12.8 \pm 0.1$ nm, $\sigma = 0.28 \pm 0.01$ and specific surface area of 200 m²/g. The nanocomposites with a silica fraction of 15 vol.% were prepared by solution blending in purified H_2O and subsequent freeze drying to achieve a good particle dispersion.

SANS experiments were performed at KWS-2 of the JCNS at the FRM II in Garching, Germany, at a temperature of $T = 413$ K. Details of these experiments are found in the Supplemental Material [13]. The dynamic experiments were performed at the neutron spin echo instrument IN15 at the Institute Laue-Langevin in Grenoble again at $T = 413$ K. Furthermore, high resolution neutron time-of-flight experiments were carried out at the TOFTOF instrument of the FRM II in Garching covering a temperature range from 343 to 443 K.

Figure 1 displays NSE results on a pure PEG-$(OH)_2$ melt for various Q values. The figure evidences that for small Q the internal dynamics (dashed lines) is not contributing to the signal. At $Q = 0.05$ Å^{-1} solely translational diffusion is measured. Only at $Q = 0.2$ Å^{-1} is the experiment
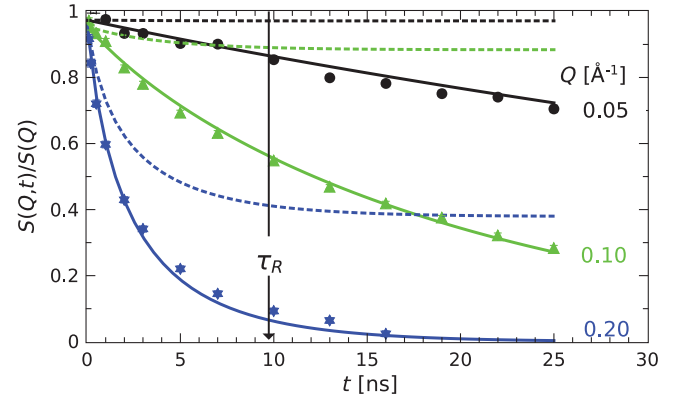

FIG. 1 (color). The intermediate scattering function of the pure PEG (OH) sample measured at 413 K. The solid lines show the full Rouse model fits, the dashed lines indicate the sole contribution from the internal chain relaxation modes.

primarily sensitive to internal motions as there is a significant contribution from the internal dynamics for times up to $\tau_R = 9.7 \pm 0.1$ ns. We note that the dynamics in the pure melt is independent of the choice of end groups.

Figure 2 compares NSE results for three exemplary Q values from the nanocomposites containing PEG chains with either OH or CH_3 end groups. The solid and dashed lines are fit results to be discussed later. The dotted lines give the pure melt reference. The inset evidences that the initial decay of $S(Q,t)$ and thus the basic Rouse rate W is unaffected by the silica. Overall we recognize that the effect of SiO_2 nanoparticles on the PEG melts depends significantly on the end group. Let us first consider the $Q = 0.05$ Å^{-1} data where translational diffusion is measured. Obviously in going from the pure melt via the
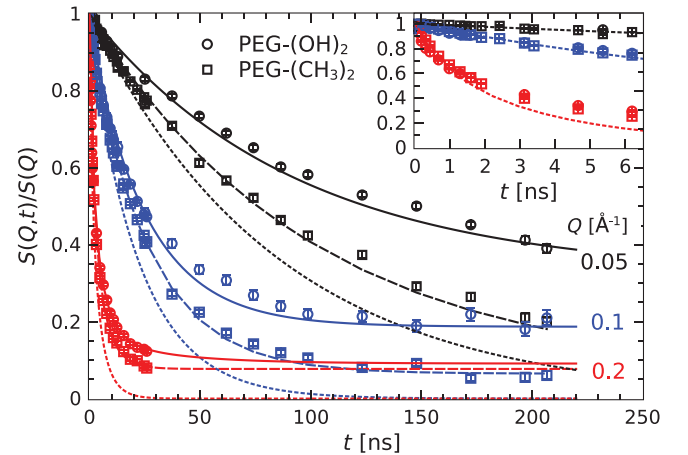

FIG. 2 (color). Comparison of the intermediate scattering functions of the two PEG-silica samples [OH (circles) and CH_3 (squares) end groups]. The pointed line represents the pure melt. The solid and dashed lines are respective model fits (see text). The inset compares the initial decay at short times for the nanocomposites and the pure melt.

PEG-$(CH_3)_2$ to the PEG-$(OH)_2$ sample, the translational diffusion appears to be increasingly retarded. At $Q = 0.1$ Å^{-1} we witness the appearance of a new phenomenon. The dynamic response of both matrices assumes a plateau at long times with a higher value for PEG-$(OH)_2$. Since the internal modes have fully relaxed in this long time regime, about an order of magnitude larger than τ_R, the formation of a plateau directly indicates the fraction of chains that are not participating in the translational diffusion [11]. These are the chains that are adsorbed at the particle surface for times much longer than 200 ns. Thereby, the OH-terminated chains are more effectively adsorbed than the methyl group terminated ones. Finally, at $Q = 0.2$ Å^{-1}, where the experiment is particularly sensitive to the long wave-length Rouse modes, we observe that for the OH-terminated chains the decay of $S(Q, t)$ goes well beyond that of the plateau observed at $Q = 0.1$ Å^{-1} signifying that the adsorbed chains undergo large scale internal dynamics. This is different for the PEG-$(CH_3)_2$ chains. Here, $S(Q, t)$ decays to the same plateau as at lower Q. Thus, the adsorbed chains are limited to at most small scale motions in the order of 1 nm [14].

Figure 3 displays exemplary results for the local chain dynamics. We compare time-of-flight spectra for pure PEG with those from nanocomposites with the OH- and CH_3-terminated matrices. At $Q = 1.5$ Å^{-1} the experiment observes very local motions as those relating to rotational motions around the covalent bonds [11]. All three spectra are characterized by a broad quasielastic peak relating to this motion. In addition, on the top of the broad peak for the nanocomposites, a small elastic peak evolves with an intensity of about 3% of the total scattering. The Q dependence of this intensity is shown in the inset and compared with the SiO_2 structure factor peak obtained from a pure

SiO_2 glass [15]. Both, estimating the SiO_2 peak intensity from the ratio of the respective cross sections as well as comparing the location of the observed peak with that of pure SiO_2, we identify the observed elastic contribution as resulting from the SiO_2 nanoparticles, possibly slightly enhanced by the incoherent scattering from the OH groups at the SiO_2 surface.

We emphasize that the elastic fraction displays only a weak temperature dependence down to 343 K very close to the crystallization temperature of PEG (see Supplemental Material [13]). We may conclude that in the nanocomposites both types of chains undergo fast picosecond dynamics that is very similar to that in the bulk. There is no indication for the hypothesized glassy polymer layer.

In the next step we quantitatively analyze the data guided by the qualitative understanding arrived at from Figs. 2 and 3. We consider a model with two chain fractions: free chains and adsorbed chains, both with the same Rouse relaxation rate W. While for the free chains the diffusion is reduced, for the adsorbed chains $D_R = 0$. The internal dynamics of the adsorbed OH chains is described by the Rouse dynamics of end-grafted chains. On the contrary, no internal chain dynamics is considered for the adsorbed fraction in the case of the CH_3-terminated chains. Thus, the fit function assumes the form

$$S(Q, t) = \alpha S(Q, t)_{\text{ad}}^{D_R=0} + (1 - \alpha)S(Q, t)_{\text{free}}, \quad (2)$$

where α is the adsorbed fraction and $S(Q, t)$ refers to Eq. (1) with the indices indicating the two different boundary conditions for the free and end-grafted chains. Note that without internal chain dynamics $S(Q, t)_{\text{ad}} = 1$. By this approach very good fits of the data are achieved [see solid (OH) and dashed (CH_3) lines in Fig. 2].

Figure 4 demonstrates the robustness of the fit results by displaying the consequences of varying one parameter keeping always the others fixed. Let us begin with the data at $Q = 0.1$ Å^{-1}, where the plateau value directly

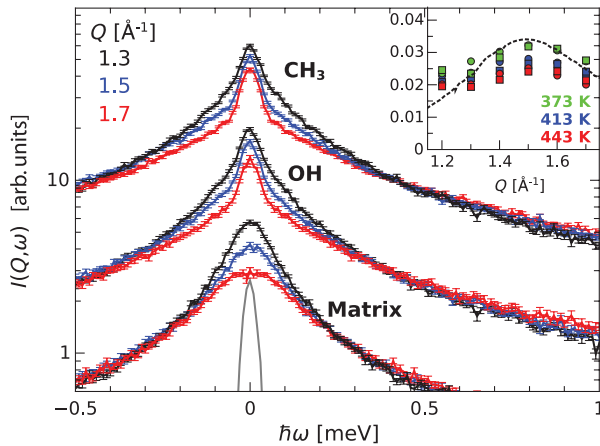FIG. 3 (color). The time-of-flight spectra of the matrix [PEG-$(OH)_2$] and both nanocomposites at 413 K compared to the resolution (thin line). The Q dependence of the intensity of the small elastic peak on top of the PEG-silica spectra is shown in the inset for three temperatures. The dashed line represents the SiO_2 structure factor.
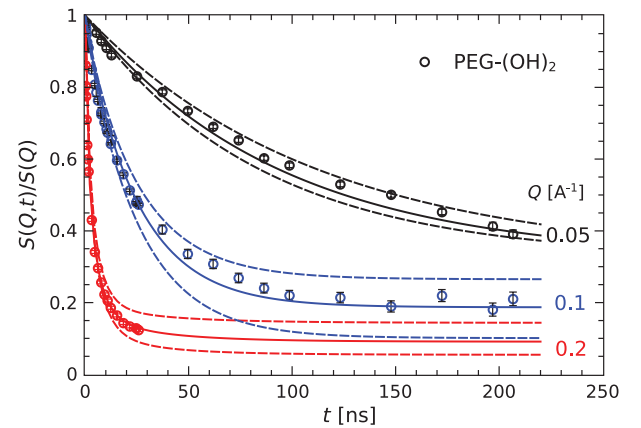

FIG. 4 (color). For the case of PEG-$(OH)_2$ at 413 K the robustness of the fit results (solid lines) is demonstrated by an explicit variation of the parameters (dashed lines).

reveals the adsorbed fraction. For PEG-$(OH)_2$ we find $\alpha = 0.21 \pm 0.02$ corresponding to about one adsorbed chain per nanometer square, a very high adsorption density that can only be realized if the majority of the chains are end-grafted. For PEG-$(CH_3)_2$ we find $\alpha = 0.06 \pm 0.01$; the chains are obviously multiply attached with the backbone.

The two blue dashed lines signify the result if we vary the adsorbed fractions to 0.1 or 0.3. With $\alpha = 0.21$ fixed we may now inspect the reduction of the diffusion coefficient. The best fit gives $D = f D_{R,\text{free}}$ with $f = 0.90 \pm 0.03$. The two dashed black lines display the results for an unchanged diffusion coefficient and $f = 0.75$. We note that the found reduction by 10% corresponds well to the value found for a purely repulsive nanocomposite containing nanoparticles of comparable size [16]. Finally we consider the highest Q value that is particularly sensitive to the internal chain dynamics [11]. The lower dashed line represents the expectation for an end-grafted chain that is allowed to freely explore its half space [12]. This gives rise to a too strong decay of the structure factor. However, with the high grafting density given here the freedom of the chain motion will be restricted. Therefore, we reduced the motional amplitudes in Eq. (1) by a common factor resulting in a reduction of the amplitudes of motions on average by a factor of 2. A further amplitude reduction by another factor 2 would lead to the upper dashed line.

Let us now rationalize the results. For the OH-terminated chains we have an adsorbed fraction that corresponds close to about one chain per square nanometer SiO_2 surface. These chains undergo large scale mobility and may be well approximated by an end-tethered PEG chain that follows the Rouse model for grafted chains if the motional amplitudes are reduced by an overall factor of 2 (crowding). Thus, we may conclude that a large majority of chains are grafted at the SiO_2 surface and lead to a micellelike structure of the nanoparticle. Thereby, the fixation time of the chains must be much longer than the observation time of the experiments ($\tau_{\text{ad}} \gg 200$ ns). This means that the binding energy must be very significant. From a simple Boltzmann argument it would have to be larger than 40 kJ/mol pointing toward the direction of a chemical or at least a very strong hydrogen bond. For the CH_3-terminated chains we find a much weaker chain adsorption of only 6% with no visible large scale internal dynamics within the adsorbed fraction. The Q plateaus at $Q = 0.2$ Å^{-1} and $Q = 0.1$ Å^{-1} are identical. Both from equating the amount of chains with the surface as well as calculating the maximum amplitude of motion that would be invisible at $Q = 0.2$ Å^{-1} (see Ref. [14]) we arrive at an apparently immobilized layer of close to 1 nm thickness. This layer however, is locally very mobile. The results of unchanged local dynamics is also corroborated by dielectric spectroscopy in PMMA- and PVAc-silica nanocomposites [17,18].

Our detailed dynamic neutron results thus enhance significantly the microscopic insight into the polymer chain dynamics in attractive nanocomposites. From the greatly different behavior of the CH_3- and OH-terminated PEGs we have realized that for the PEG-OH system the mean field approaches such as the polymer reference interaction site model are not applicable. There an average binding energy of $0.5 k_B T$ is predicted that needs to be related with the value well surpassing $10 k_B T$ found here. This binding energy, however, is concentrated at a single point. Another aspect concerns the often invoked glassy layer around nanoparticles. The neutron time-of-flight experiments unambiguously show that at the same temperature with the same SiO_2 surface the PEG undergoes picosecond dynamics while from the NMR line shape a glassy layer was concluded [4]. The neutron data tell about the existence of a confined polymer layer that however is internally highly mobile and not glassy at all. This result should stimulate a reinterpretation of many earlier results and further enhance the understanding of nanocomposites. Also to our knowledge none of the computer simulations have yet considered the highly significant role of chain termination in the understanding of attractive nanoparticles.

---

*g.j.schneider@fz-juelich.de

[1] Q. Zhang and L. A. Archer, Langmuir **18**, 10435 (2002).

[2] A. S. Sarvestani and C. R. Picu, Polymer **45**, 7779 (2004).

[3] B. J. Anderson and C. F. Zukoski, Macromolecules **41**, 9326 (2008).

[4] S. Y. Kim, H. W. Meyer, K. Saalwächter, and C. F. Zukoski, Macromolecules **45**, 4225 (2012).

[5] K. U. Kirst, F. Kremer, and V. M. Litvinov, Macromolecules **26**, 975 (1993).

[6] L. M. Hall, B. J. Anderson, C. F. Zukoski, and K. S. Schweizer, Macromolecules **42**, 8435 (2009).

[7] Y. Huang and M. M. Santore, Langmuir **18**, 2158 (2002).

[8] S. Y. Kim, K. S. Schweizer, and C. F. Zukoski, Phys. Rev. Lett. **107**, 225504 (2011).

[9] N. Jouault, F. Dalmas, S. Said, E. Di Cola, R. Schweins, J. Jestin, and F. Boué, Phys. Rev. E **82**, 031801 (2010).

[10] A. Papon, H. Montes, M. Hanafi, F. Lequeux, L. Guy, and K. Saalwächter, Phys. Rev. Lett. **108**, 065702 (2012).

[11] D. Richter, M. Monkenbusch, A. Arbe, and J. Colmenero, *Neutron Spin Echo in Polymer Systems*, Advances in Polymer Science Vol. 174 (Springer, Berlin, Heidelberg, 2005).

[12] L. Willner, R. Lund, M. Monkenbusch, O. Holderer, J. Colmenero, and D. Richter, Soft Matter **6**, 1559 (2010).

[13] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.110.178001 for details on the experiments and data analysis.

[14] An estimation on the basis of the reptation confinement $[1 - \exp(-Q^2 s^2 / 36)]$ with s the dynamic confinement size gives $s \approx 1$ nm.

[15] S. Susman, K. J. Volin, D. G. Montague, and D. L. Price, Phys. Rev. B **43**, 11076 (1991).

[16] G. J. Schneider, K. Nusser, S. Neueder, M. Brodeck, L. Willner, B. Farago, O. Holderer, W. J. Briels, and D. Richter, Soft Matter **9**, 4336 (2013).

[17] V. M. Boucher, D. Cangialosi, A. Alegría, J. Colmenero, J. Gonzáles-Irun, and L. M. Liz-Marzan, Soft Matter **6**, 3306 (2010).

[18] R. B. Bogoslovov, C. M. Roland, A. R. Ellis, A. M. Randall, and C. G. Robertson, Macromolecules **41**, 1289 (2008).