602 *Chem. Mater.* **2000,** *12,* 602−604

Cross-Linking of Poly(methyl methacrylate) by the Methacrylate-Substituted Oxozirconium Cluster $Zr_6(OH)_4O_4(Methacrylate)_{12}$

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Received November 15, 1999
Revised Manuscript Received January 18, 2000

There is increasing interest in a new class of inorganic−organic copolymers that is characterized by the covalent incorporation of structurally well-defined oxometalate clusters in organic polymers. In silicon chemistry, polymers with interesting properties were obtained by reinforcing or cross-linking organic polymers by the cubic $R_8Si_8O_{12}$ clusters, in which one[1] or more[2] of the organic substituents R contains a polymerizable group. Copolymerization of $Bu_{12}Sn_{12}O_{14}(OH)_6(OMc)_2$ (OMc = methacrylate) with methyl methacrylate resulted in only little cross-linking, the stannate clusters acting mainly as terminating units.[3] In addition to the properties observed for $R_8Si_8O_{12}$-reinforced systems, the incorporation of transition metal oxo clusters could allow interesting modifications of the optical properties of the polymers and the preparation of polymers with special magnetic or catalytic properties.

In this Communication, we report preliminary results on the cross-linking of poly(methyl methacrylate) by the oxozirconium methacrylate cluster $Zr_6(OH)_4O_4(OMc)_{12}$ (**1**). In a series of recently described crystalline oxozirconium methacrylate clusters,[4] **1** had the closest structural similarity to zirconia. It consists of a $Zr_6O_4(OH)_4$ core in which the faces of a Zr_6 octahedron are alternatively capped by μ_3-O and μ_3-OH groups. The cluster can be considered the smallest possible piece of tetragonal zirconia wrapped by methacrylate ligands. Three of them chelate the zirconium atom at one triangular face, while the remaining nine bridge the other edges. Inspection of the crystal structure of **1** shows that the double bonds of the methacrylate ligands should be fully accessible for chemical reactions.

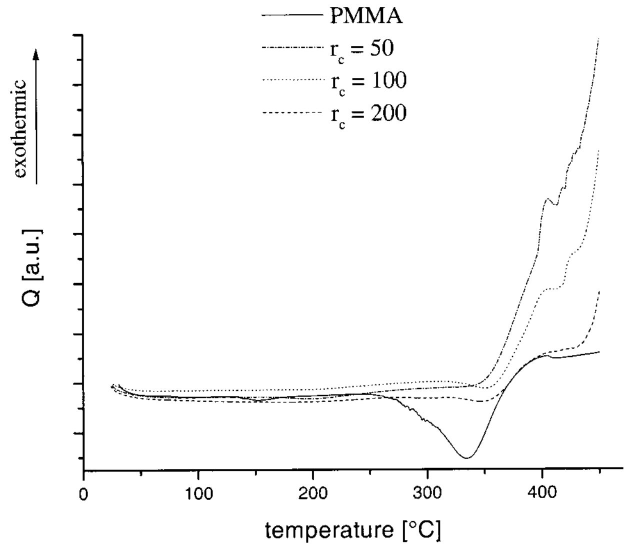

Figure 1. Differential scanning calorimetry of undoped PMMA and the copolymers with $r_c = 50$, 100, and 200.

Radical-initiated polymerization of **1** with a 50- to 200-fold excess of methyl methacrylate in benzene gave copolymers that still contained 25−30 wt% of benzene after drying at reduced pressure.[5] Residual benzene was removed by extraction with ethyl acetate. After removal of the solvent, transparent glassy polymers were obtained; only the polymer prepared with a 1:50 ratio of **1** and methyl methacrylate was slightly opaque. The appearance of the polymers did not change when stored in ambient atmosphere for prolonged periods of time. The swelling behavior of the cluster-doped polymers in ethyl acetate shows a clear dependence on the methyl methacrylate/**1** molar ratio (r_c). While undoped poly(methyl methacrylate) (PMMA) dissolves, the copolymers only swell and take up 1.04, 1.65, and 2.90 g of the solvent per gram of the copolymer within 3 days (r_c = 50, 100, and 200, respectively). This linear relationship clearly shows that the cross-linking density is increased with an increasing portion of **1**.

TGA analysis of undoped PMMA in air shows that the polymer completely decomposes between 350 and 400 °C. The onset of the thermal decomposition of the copolymers is slightly (10−20°) shifted to higher temperatures. The DSC curves are shown in Figure 1. While undoped PMMA depolymerizes prior to decomposition,

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(1) For example: Schwab, J. J.; Lichtenhan, J. D.; Chaffee, K. P.; Mather, P. T.; Romo-Uribe, A. *Mater. Res. Soc. Symp. Proc.* **1998**, *519*, 21. Lichtenhan, J. D.; Haddad, T. S.; Schwab, J. J.; Karr, M. J.; Chaffee, K. P.; Mather, P. T. *Polym. Prepr.* **1998**, *39* (1), 489.

(2) For example: Sellinger, A.; Laine, R. M. *Macromolecules* **1996**, *29*, 2327. Lin, E. K.; Snyder, C. R.; Mopsik, F. I.; Wallace, W. E.; Wu, W. L.; Zhang, C. X.; Laine, R. M. *Mater. Res. Soc. Symp. Proc.* **1998**, *519*, 15.

(3) Ribot, F.; Banse, F.; Sanchez, C.; Lahcini, M.; Jousseaumme, B. *J. Sol-Gel Sci. Technol.* **1997**, *8*, 529. Angiolini, L.; Caretti, D.; Carlini, C.; De Vito, R.; Niesel, F. T.; Salatelli, E.; Ribot, F.; Sanchez, C. *J. Inorg. Organomet. Polym.* **1998**, *7*, 151.

(4) (a) Kickelbick, G.; Schubert, U. *Chem. Ber.* **1997**, *130*, 473. (b) Kickelbick, G.; Wiede, P.; Schubert, U. *Inorg. Chim. Acta* **1999**, *284*, 1.

(5) To a solution of 2.62 g (26.2 mmol) of methyl methacrylate (filtered over alumina to remove the stabilizer) and 0.91 g (0.54 mmol) of **1** in 6 mL of benzene was added 21 mg (0.09 mmol) of dibenzoyl peroxide. When heated to 65 °C, the solution became turbid after 2−3 h and then solidified. Heating was continued for 9−10 h, and then the solvent was removed at 70 °C/8 mbar. The remaining benzene was extracted with ethyl acetate, and then the solvent was again removed under reduced pressure. The samples with a methyl methacrylate/cluster ratio of 100:1 and 200:1 were analogously prepared, keeping the methyl methacrylate:initiator:solvent ratio constant. Elemental analyses of the polymers (the theoretical values refer to complete incorporation of both methyl methacrylate and **1**). For, r_c = 50: Found: C, 51.68; H, 7.01. Calcd: C, 53.41; H, 6.95. For, r_c = 100: Found: C, 56.03; H, 7.67. Calcd: C, 56.32; H, 7.41. For, r_c = 200: Found: C, 57.82; H, 8.15. Calc.: C, 58.03; H, 7.70.

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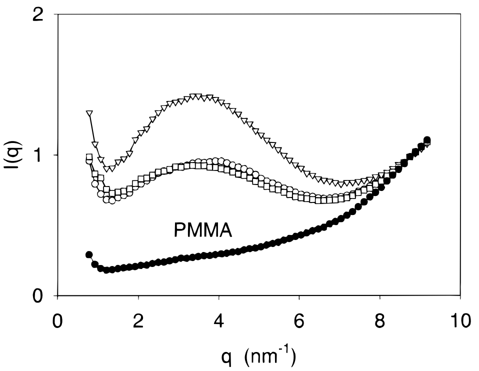

Figure 2. SAXS data $I(q)$ from the copolymers with $r_c = 50$, 100, and 200 (open circles, triangles, and squares, respectively). The full symbols correspond to SAXS data from undoped PMMA. All data were normalized to $I(q) = 1$ at $q = 0.9$ nm^{-1}, which corresponds to the assumption that PMMA dominates the X-ray scattering signal at larger q values.

this behavior is distinctly less pronounced for the copolymers with $r_c = 100$ and 200, and disappears for the copolymer with $r_c = 50$. The mass of the solid residue in the TGA experiments upon heating the polymers to 800 °C in air ($r_c = 50$, 7.41%; $r_c = 100$, 6.33%; $r_c = 200$, 3.06% of the initial mass) corresponds very well to the ZrO_2 content of the starting mixture (theoretical values for $r_c = 50$, 8.18%; $r_c = 100$, 6.23%; $r_c = 200$, 3.37%) (see Supporting Information). This shows that neither methyl methacrylate nor **1** (or parts of **1**) was lost during polymerization or workup.

Small-angle scattering experiments[6,7] were performed to find out whether clusters are retained in the polymeric material. Figure 2 shows the scattering curves, $I(q)$, of the copolymers together with the scattering curve of undoped PMMA, all normalized to 1 at $q = 9$ nm^{-1}.[8]

In a next step, the signal from PMMA, $I_{PMMA}(q)$, was subtracted from the data. Figure 3 shows plots of $J(q) = [I(q) - I_{PMMA}(q)]/I_0$, where I_0 is a constant chosen to obtain coincidence of the data at large q values. It is apparent from Figure 3 that this coincidence extends over a range of q values, in which the data can be represented by $F(q) = \exp(-q^2R^2/5)$, where $R = 0.49$ nm. At small q values, the scattering curves depend slightly on r_c. The interpretation of this effect is that in all three samples the structure is composed of identical units whose packing, however, is different. The shape of $F(q)$ is compatible with nearly spherical units having a radius of $R = 0.49$ nm. The existence of a maximum in the SAXS function indicates some kind of short-range order in the arrangement of the spherical units. For randomly packed spheres with a diameter D (hard-sphere model), an approximate scattering function is the Zernicke–Prins–Debye expression,[9] $I(q) = F(q)\,[1 - \nu nS(q)]^2$, with n = number of clusters per unit volume, and $\nu = 4\pi D^3/3$. $S(q)$ is the scattering amplitude of a sphere and a rough approximation is $S(q) = \exp(-q^2D^2/10)$.[6] In the original hard-sphere model $D = 2R$, but if the repulsion radius of the spheres is somewhat larger than the spherical cluster itself, then it is possible that $D > 2R$. We have fitted our SAXS results with R, D, and n as free parameters. We obtained for all three samples $R = 0.49$ nm and $D = 1.03-1.10$ nm which is, indeed, somewhat larger than $2R$. The number of clusters per unit volume, n, decreased from 12.5×10^{19} clusters/cm^3 in the sample with $r_c = (50-10.5) \times 10^{19}$ clusters/cm^3 in the two other samples.

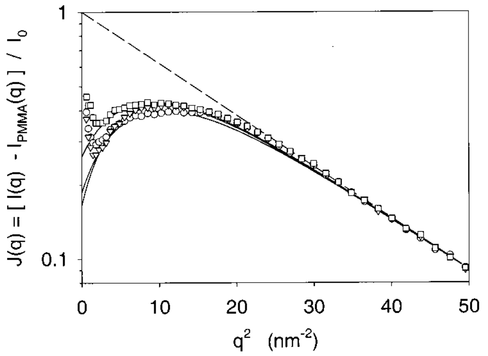

Figure 3. SAXS data from Figure 2 after subtraction of the signal from PMMA, $I_{PMMA}(q)$, and renormalization by an empirical factor I_0. I_0 was chosen such as to obtain identical SAXS intensities at large q values. The resulting curves $I(q)$ should be proportional to the true SAXS signal from Zr clusters after removal of the scattering from excess PMMA. The symbols are defined as in Figure 2. The x axis corresponds to the square of the scattering vector, q^2, and the y axis to $J(q)$ in a logarithmic scale (Guinier plot). The straight line represents the function $\exp(-q^2R^2/5)$ with $R = 0.49$ nm. The full lines are separate fits to the three data sets as explained in the text.

Hence, the fits clearly showed that the microstructure of all cluster-doped samples can be described by a hard-sphere packing of identical spherical clusters. The value of R and D have to be compared to the diameter of **1**. As an estimate of the size of the isolated cluster, the distance between two methacrylic double bonds (bridging carboxylate ligands) across the cluster can be taken, which is 1.24 nm.[4a] Hence, D could be interpreted as the outer diameter of the cluster. R would be the effective radius of this same cluster, but where all elements have to be weighted with their respective number of electrons. Since the heaviest elements (Zr) are sitting fairly deep inside the cluster (including ligands), it is clear that the resulting effective radius is smaller than half the outer diameter. According to our model, n decreases with a decreasing portion of the clusters in the copolymer, but not as strongly as would be anticipated. Moreover, n is less than a factor of 10 below the limit resulting from tight packing of the spheres. This unexpected phenomenon can be interpreted as an aggregation of the clusters corresponding to a microphase separation. The reason for this could be preferred homopolymerization of **1**.

In conclusion, we have shown that copolymerization of the oxozirconium cluster **1** with methyl methacrylate results in materials in which cluster units cross-link the polymer chains. How many of the methacrylate ligands of **1** are used for cross-linking is currently unknown.[10] Inorganic–organic hybrid polymers with zirconium oxide components have previously been made from $Zr(OR)_4$ modified by polymerizable organic ligands such

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(6) Guinier, A.; Fournet, G. *Small-Angle Scattering of X-rays*; J. Wiley & Sons: New York, 1955.

(7) Hüsing, N.; Schubert, U.; Misof, K.; Fratzl, P. *Chem. Mater.* **1998**, *10*, 3024.

(8) It is assumed that scattering is dominated by that of PMMA at this length.

(9) Zernicke, F.; Prins, J. A. *Z. Phys.* **1927**, *41*, 184. Debye, P. *Phys.. Z.* **1927**, *28*, 135, see also ref 6.

as 2-hydroxyethyl methacrylate.[11] These polymers may be related to the ones described here. However, the inorganic structures formed in the alkoxide systems were not identified and are probably not uniform in size. Our approach is basically a two-step process. In the first step, the structurally well-defined oxo clusters are prepared by carefully controlled hydrolysis of methacrylate-substituted $Zr(OR)_4$. The clusters are then copolymerized with organic monomers in the second. The thus obtained hybrid polymers are doped with covalently bonded uniform zirconium oxide nanoparticles.

Acknowledgment. We thank W. Tesch for his help in performing the SAXS experiments and Dr. Nicola Hüsing for the MAS NMR spectrum. Financial support by the Fonds zur Förderung der wissenschaftlichen Forschung (FWF), Austria, is gratefully acknowledged.

Supporting Information Available: Original SAXS curves, TGA curves, and ^{13}C MAS NMR spectrum of the polymer with $r_c = 100$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) The solid-state ^{13}C NMR spectrum of the polymer with $r_c = 100$ shows a very weak group of signals at about 140 ppm, which is the typical range of unreacted $=CH_2$ groups (see Supporting Information). However, this signal does not allow the portion of unreacted methacrylate units of **1** to be quantified.

(11) Di Maggio, R.; Fambri, L.; Guerriero, A. *Chem. Mater.* **1998**, *10*, 1777. Sanchez, C.; In, M. *J. Non-Cryst. Solids* **1992**, *147/148*, 1. In, M.; Gerardin, C.; Lambard, J.; Sanchez, C. *J. Sol-Gel Sci. Technol.* **1995**, *5*, 101.