

# Swelling behavior and thermal stability of poly(methylmethacrylate) crosslinked by the oxozirconium cluster $Zr_4O_2(\text{methacrylate})_{12}^{\dagger}$

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**A new isomer of the oxozirconium cluster  $Zr_4O_2(\text{methacrylate})_{12}$  was obtained by reaction of zirconium butoxide with an excess of methacrylic acid. Contrary to the known isomer, the structure is centrosymmetric with a planar, rhombic  $Zr_4$  core. Copolymerization with a 56–207-fold excess of methylmethacrylate results in cluster-crosslinked poly(methylmethacrylate) that swells in ethyl acetate but does not dissolve. The solvent uptake during swelling decreases and the thermal stability improves with an increasing portion of the cluster. Copyright © 2001 John Wiley & Sons, Ltd.**

**Keywords:** inorganic–organic hybrid materials; poly(methylmethacrylate); oxozirconium clusters; zirconium compounds; sol–gel processing; zirconium alkoxides; thermal decomposition; swelling of polymers; X-ray structure analysis

## INTRODUCTION

The so-called POSS-reinforced polymers (POSS: polyhedral oligomeric silsequioxanes) have gained much interest as a new class of inorganic–organic hybrid materials. They are characterized by the covalent incorporation of structurally well-defined organosilicate clusters in organic polymers and are prepared by copolymerization of organic mono-

mers with mainly the cubic  $R_8Si_8O_{12}$  clusters, in which one<sup>1</sup> or more<sup>2</sup> of the organic substituents R contains a polymerizable group.

We have recently reported a first example in which this approach was extended to transition-metal oxo clusters. In addition to the properties observed for  $R_8Si_8O_{12}$ -reinforced systems, the incorporation of transition-metal clusters in general could allow interesting modifications of the optical properties of the polymers and the preparation of polymers with special magnetic or catalytic properties.

Our approach to the preparation of the new inorganic–organic hybrid materials is basically a two-step process. In the first step, the structurally well defined oxo clusters are prepared by carefully controlled hydrolysis and condensation of methacrylate-substituted  $Zr(OR)_4$ . The water is generated *in situ* by an esterification reaction. Depending on the methacrylic acid/ $Zr(OR)_4$  ratio employed, clusters of different size crystallize in nearly quantitative yields from the reaction mixtures.<sup>3</sup> The methacrylate-substituted clusters are then copolymerized with organic monomers. In a previous article, we have described the copolymerization of 0.5–2 mol% of the methacrylate-substituted oxozirconium cluster  $Zr_6(OH)_4O_4(OMc)_{12}$  (OMc = methacrylate) (**1**) with methylmethacrylate.<sup>4</sup> The glassy, highly transparent hybrid polymers obtained contain covalently bonded clusters that may be considered structurally well defined zirconium oxide nanoparticles of uniform size. Small-angle x-ray scattering measurements confirmed that the clusters were retained in the polymer. The properties of the polymers indicate that the clusters crosslink the poly(methylmethacrylate) (PMMA) chains.

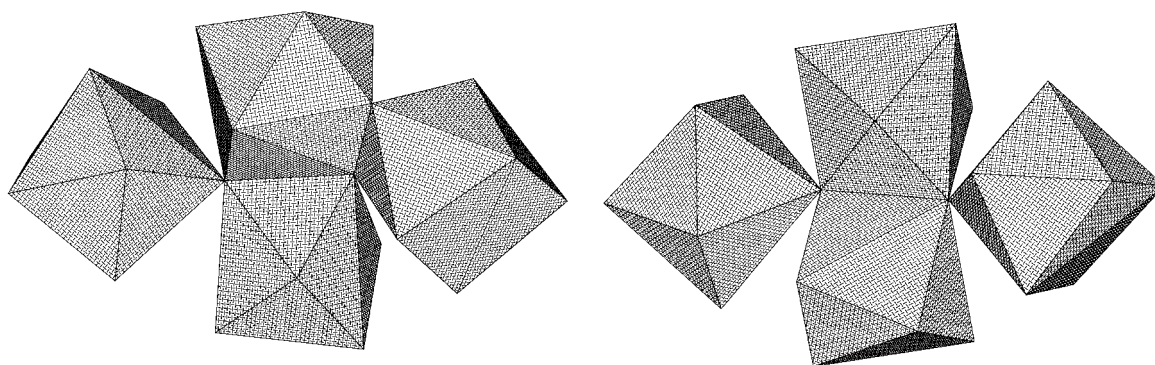
In this paper we describe the extension of our previous study with  $Zr_6(OH)_4O_4(OMc)_{12}$  (**1**) as the cluster component to the use of  $Zr_4O_2(OMc)_{12}$  (**2**). The  $Zr_4$  cluster has the advantage of a less time-consuming synthesis, as we will describe in this article.

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**Figure 1** Linkage of the coordination polyhedra in **2a** (left) and **2b** (right). Both compounds have the same chemical composition ( $\text{Zr}_4\text{O}_2(\text{OMc})_{12}$ ).

## RESULTS AND DISCUSSION

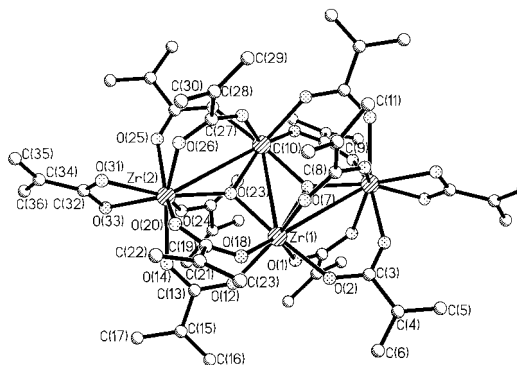
We had previously obtained crystalline  $\text{Zr}_4\text{O}_2(\text{OMc})_{12}$  (**2a**) by reaction of a 70% solution of  $\text{Zr}(\text{OPr})_4$  in propanol with a 15-fold excess of methacrylic acid after 7 days.<sup>3</sup> The time required for crystallization from the reaction mixture can be considerably shortened by reacting  $\text{Zr}(\text{OPr})_4$  in propanol or  $\text{Zr}(\text{O}i\text{Bu})_4$  in butanol with a fourfold excess of methacrylic anhydride instead of methacrylic acid itself. Crystals of the cluster are then obtained in high yield in 1–2 days.

The four zirconium atoms in **2a** have a distorted butterfly arrangement, with a dihedral angle between the two  $\text{Zr}_3$  planes of  $9.7^\circ$ . The  $\text{Zr}_3$  triangles are capped by a  $\mu_3$ -oxygen atom from different sides. Two of the methacrylate ligands are chelating and the other ten bridge the  $\text{Zr}$ – $\text{Zr}$  edges (except the intra-annular  $\text{Zr}$ – $\text{Zr}$ ). The most prominent feature of the structure of **2a** is its asymmetry (Fig. 1), which is induced by one methacrylate ligand being in the rare  $\eta^2, \mu_2$ -coordination mode with one of the oxygen atoms of a chelating carboxylate group additionally coordinated to another metal atom.

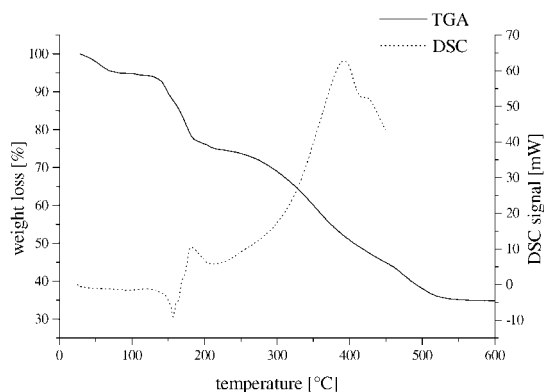
We now obtained a cluster (**2b**) with the same composition as **2a** but a slightly different crystal structure, starting from zirconium butoxide and a sevenfold excess of methacrylic acid. Crystals of **2b** precipitated from the reaction mixture in 1 day in high yield. The general structure of cluster **2b** is very similar to that of **2a** (Figs 1 and 2), except that it is symmetric with a crystallographic inversion symmetry, i.e. the four zirconium atoms are coplanar. The main difference is that the  $\eta^2, \mu_2$ -coordinated methacrylate ligand in the isomer **2a** is converted to a ‘normal’  $\mu_2$ -bridge in **2a**. As a result,

both central  $\text{Zr}(1)$  atoms are seven-coordinate (neglecting the  $\text{Zr}$ – $\text{Zr}$  interaction), whereas the outer  $\text{Zr}(2)$  atoms are eight-coordinate. The  $\text{Zr}(1)$ – $\text{Zr}(1A)$  distance is shortened (329.45(6) pm) relative to **2a** (335.32(6) pm). The solution NMR of **2a** and **2b** are the same, indicating that the structures interconvert in solution, as expected, and that the different solid-state structures are just due to the different reaction conditions (the crystals precipitate from the reaction mixture).

The thermal decomposition of **2b** was investigated by thermogravimetric analysis (TGA) and



**Figure 2** Structure of the symmetric isomer of  $\text{Zr}_4\text{O}_2(\text{OMc})_{12}$  (**2b**). The label ‘A’ refers to symmetry-equivalent atoms (inversion symmetry).  $\text{Zr}(1)$ – $\text{Zr}(1A)$  329.45(6),  $\text{Zr}(1)$ – $\text{Zr}(2)$  366.50(5),  $\text{Zr}(1)$ – $\text{O}(23)$  205.2(2),  $\text{Zr}(1A)$ – $\text{O}(23)$  211.2(2),  $\text{Zr}(2)$ – $\text{O}(23)$  206.5(2),  $\text{Zr}(1)$ – $\text{O}(2)$  216.0(3),  $\text{Zr}(1)$ – $\text{O}(1)$  217.1(3),  $\text{Zr}(1)$ – $\text{O}(7)$  216.6(2),  $\text{Zr}(1)$ – $\text{O}(12)$  217.4(3),  $\text{Zr}(1)$ – $\text{O}(18)$  217.3(3),  $\text{Zr}(2)$ – $\text{O}(14)$  217.7(3),  $\text{Zr}(2)$ – $\text{O}(25)$  220.1(3),  $\text{Zr}(2)$ – $\text{O}(26)$  221.6(3),  $\text{Zr}(2)$ – $\text{O}(20)$  222.5(3),  $\text{Zr}(2)$ – $\text{O}(24)$  221.8(3),  $\text{Zr}(2)$ – $\text{O}(31)$  224.7(2),  $\text{Zr}(2)$ – $\text{O}(33)$  226.8(2) pm.  $\text{Zr}(1)$ – $\text{O}(23)$ – $\text{Zr}(1A)$   $104.6(1)^\circ$ ,  $\text{Zr}(1)$ – $\text{O}(23)$ – $\text{Zr}(2)$   $132.2(1)^\circ$ ,  $\text{Zr}(1)$ – $\text{O}(23)$ – $\text{Zr}(2A)$   $122.6(1)^\circ$ .



**Figure 3** TGA and DSC of  $\text{Zr}_4\text{O}_2(\text{OMc})_{12}$  (**2b**).

differential scanning calorimetry (DSC) (Fig. 3). The TGA is characterized by three well-defined stages. The first weight loss ( $-5.3\%$ ) in the temperature range  $50\text{--}100\text{ }^\circ\text{C}$  is probably due to the evaporation of residual butanol. A further weight decrease ( $-19.6\%$ ), observed in the range  $100\text{--}200\text{ }^\circ\text{C}$ , was ascribed to the cleavage and combustion of methacrylic acid. This corresponds to an endothermic event at  $157\text{ }^\circ\text{C}$  followed by an exothermic event at  $182\text{ }^\circ\text{C}$  in DSC. The final decomposition was observed in the range  $200\text{--}600\text{ }^\circ\text{C}$ , in which a gradual and continuous weight loss ( $-39.9\%$ ) was observed concomitant with a strong exothermic feature peaked at  $392\text{ }^\circ\text{C}$  in DSC.

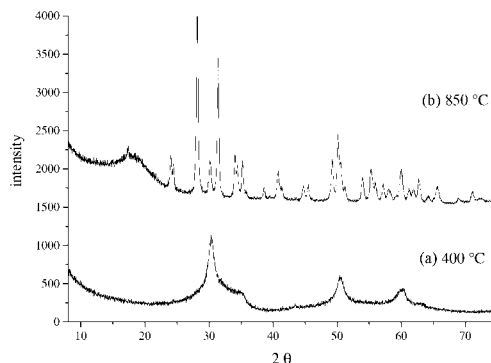
The thermal oxidation of **2b** was also studied by X-ray diffraction (XRD) (Fig. 4). A sample was placed in a ceramic vessel, heated to  $400\text{ }^\circ\text{C}$  and held at this temperature for 90 min. The XRD pattern then showed the presence of only the tetragonal phase of  $\text{ZrO}_2$ . The average crystallite size was estimated to be  $<10\text{ nm}$  from the width of the reflections (using the Scherrer equation). The formation of tetragonal instead of monoclinic zirconia, which is the stable modification at this temperature under equilibrium conditions, has already been observed and is extensively reviewed in the literature. When the crystallite size is reduced, the contribution of the surface energy to the total energy becomes more important. Below a characteristic critical crystallite size, the tetragonal phase should be more stable than the monoclinic. This critical size, which was shown to be temperature dependent,<sup>5</sup> was estimated to be  $10\text{ nm}$  at room temperature.<sup>6</sup>

The formation of the tetragonal phase upon calcination of **2b** could also be due to organic

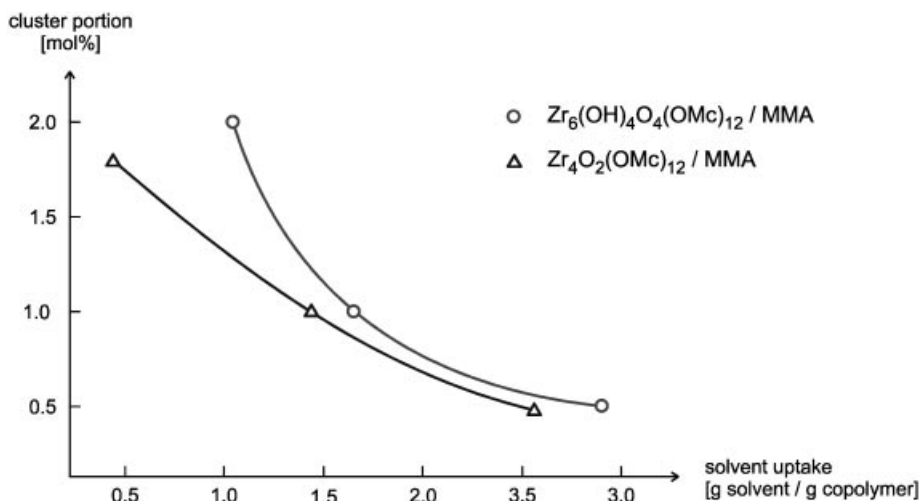
impurities.<sup>7</sup> The brown color of the sample after annealing at  $400\text{ }^\circ\text{C}$  can be ascribed to the presence of organic residuals and is in agreement with this hypothesis. When the same sample was further heated to  $850\text{ }^\circ\text{C}$  and held at this temperature for 90 min, it became colorless. The XRD pattern (trace b in Fig. 4) then showed a mixture of the monoclinic and tetragonal phases with an average particle size of about  $50\text{ nm}$ .

Radical-initiated copolymerization of **2b** with 56 to 207 molar equivalents of methylmethacrylate ( $r_c$  is the molar ratio methylmethacrylate/**2b**) in benzene gave materials that still contained some benzene after drying at reduced pressure. Residual benzene was removed by extraction with ethyl acetate. The appearance of the copolymers after removal of the solvent depended on the portion of incorporated cluster. For a high cluster portion ( $r_c = 56$ ), a white solid was obtained, whereas lower cluster contents ( $r_c = 100$  and  $207$ ) led to transparent glassy polymers. The reason for the different appearance is currently unknown; it could be due to a different degree of crosslinking among the clusters, which should increase with a higher cluster content.

The swelling behavior of the cluster-doped polymers in ethyl acetate shows a clear dependence on the methylmethacrylate / **2b** molar ratio  $r_c$ . While undoped PMMA dissolves, the copolymers only swell and take up  $0.44\text{ g}$ ,  $1.44\text{ g}$  and  $2.56\text{ g}$  of the solvent per gram of the copolymer within 3 days (for  $r_c = 56$ ,  $100$  and  $207$ , respectively). This relationship clearly shows that the crosslinking density is increased with an increasing portion of **2b**. In Fig. 5, the swelling behavior is compared with that of the copolymers prepared from  $\text{Zr}_6(\text{O-H})_4\text{O}_4(\text{OMc})_{12}$ .<sup>4</sup> Interestingly, the polymers swell



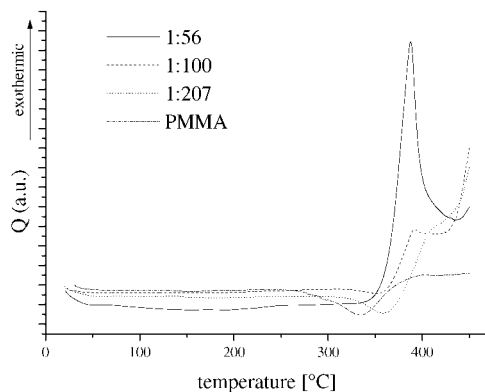
**Figure 4** XRD of  $\text{ZrO}_2$  obtained by calcination of **2b** at  $400$  and  $850\text{ }^\circ\text{C}$ . Trace b is shifted by  $1500$  intensity units.



**Figure 5** Swelling of the cluster-doped polymers in ethyl acetate.

less when **2b** is the cluster component. This could indicate that the crosslinking efficiency of **2b** is somewhat higher than that of  $\text{Zr}_6(\text{OH})_4\text{O}_4(\text{OMc})_{12}$ , possibly due to the more open and flatter structure of **2b**. Note that a polymer doped by 1 mol% of the clusters contains about 4.2 wt% of  $\text{ZrO}_2$  when crosslinked by **2b** but about 6.2 wt% of  $\text{ZrO}_2$  when crosslinked by  $\text{Zr}_6(\text{OH})_4\text{O}_4(\text{OMc})_{12}$ , due to the different number of zirconium atoms in the cluster. This could, *inter alia*, result in the possibility to modulate the optical properties at a comparable crosslinking density. The optical properties should depend on the metal oxide loading.

The thermal behavior of the copolymers was compared with that of an undoped PMMA sample



**Figure 6** DSC of undoped PMMA and the copolymers with  $r_c = 56, 100$  and  $207$ .

prepared under the same conditions (Fig. 6). DSC of undoped PMMA shows an endothermic event at  $330\text{ }^\circ\text{C}$  that is ascribed to depolymerization reactions.<sup>8</sup> An analogous endothermic event was also observed in the sample with  $r_c = 200$  having a high monomer:cluster ratio. However, this endothermic event is shifted by about 30 K to higher temperatures relative to undoped PMMA, thus suggesting a better thermal stability of the zirconium-based copolymer. The endothermic event ascribed to depolymerization is less pronounced in the  $r_c = 100$  sample, and it disappears completely in the  $r_c = 50$  sample.

The solid-state  $^{13}\text{C}$  NMR spectra of the polymers show very weak signals at about 185 ppm, 138 ppm and 127 ppm, which correspond to unreacted methacrylate ligands of **2** (COO,  $\text{CH}_2$  and CHMe groups, respectively). However, these signals do not allow one to quantify the portion of unreacted methacrylate units per cluster.

## CONCLUSIONS

We have shown that copolymerization of the oxozirconium cluster **2** with methylmethacrylate results in materials in which the cluster units crosslink the polymer chains. The crosslinked polymers are no longer soluble in ethyl acetate, but swell instead. The uptake of solvent is proportional to the cluster portion incorporated in the polymer. Thermal depolymerization is retarded

or even inhibited by the cluster crosslinking. The results are very similar to those reported for polymers crosslinked by  $Zr_6(OH)_4O_4(OMc)_{12}$  (**1**). The use of  $Zr_4O_2(OMc)_{12}$  (**2**) has the advantage that the cluster is prepared in a shorter period of time.

## EXPERIMENTAL

All experiments were done in an inert gas atmosphere (argon) using standard Schlenk techniques. Instrumentation: XRD, Phillips PW 1710 (Cu K $\alpha$  radiation) in Bragg Brentano geometry; TGA 50 and DSC 50 (Shimadzu), constant heating rate 5 K min<sup>-1</sup>; NMR, Bruker AC 250, 250.13 MHz (<sup>1</sup>H) or 62.86 MHz (<sup>13</sup>C), and Bruker DRX 400 (<sup>13</sup>C MAS).

### Synthesis of $Zr_4O_2(OMc)_{12}$ (**2a**) from $Zr(OPr)_4$ and methacrylic acid anhydride

4.283 g of a 70% solution of  $Zr(OPr)_4$  in *n*-propanol (9.15 mmol) were added to 6.095 g (37.2 mmol) of methacrylic acid anhydride (94%). The reaction is exothermic. The solution was allowed to stand at room temperature for 2 days, resulting in the separation of 2.66 g (yield 82%) of colorless prismatic crystals soluble in chloroform, benzene and toluene. The unit cell was identical with that of the crystals previously characterized by single-crystal X-ray crystallography.<sup>3a</sup>

<sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>, 22 °C): 6.18 (br, 12 H, CH<sub>2</sub>, *cis*-H to the carboxylate group), 5.48 (br, 12 H, CH<sub>2</sub>, *trans*-H to the carboxylate group), 1.84 (s, 36 H, CH<sub>3</sub>). Weak signals (<2%) at 4.17, 3.70, 2.10, 1.63, 1.39, 0.92 ppm are ascribed to by-products. <sup>13</sup>C{<sup>1</sup>H} NMR ( $\delta$ , CDCl<sub>3</sub>, 22 °C): 175.9 (br, COO), 137.8 (CH<sub>2</sub>C(CH<sub>3</sub>)COO), 126.8 (CH<sub>2</sub>), 17.9 (CH<sub>3</sub>) ppm. IR (CCl<sub>4</sub>): 2977 (w, CH), 2953 (w, CH), 2922 (w, CH), 1697 (m, COOH), 1644 (m, C=C), 1595 (s, br, asym. COO), 1519 (m) 1501 (w), 1460 (s, sym. COO), 1426 (s), 1373 (m), 1321 (w), 1296 (w), 1247 (m), 1202 (w, br), 1006 (w), 943 (m), 880 (w), 829 (w) cm<sup>-1</sup>. The observation of the typical COOH vibration of uncoordinated acid in the IR spectrum is in agreement with the <sup>13</sup>C NMR data, where the broad peak at 176.4 ppm suggests the existence of a fast exchange between the coordinated carboxylate groups and the presence of a small amount of free methacrylic acid in solution.

### Synthesis of $Zr_4O_2(OMc)_{12}$ (**2b**) from $Zr(OPr)_4$ and methacrylic acid

1.73 g (3.6 mmol) of an 80% solution of  $Zr(OBu)_4$  in *n*-butanol was mixed with 2.04 g (24 mmol) of methacrylic acid. The solution was then allowed to stand at room temperature for 1 day, resulting in the separation of 1.09 g (yield: 86%) of cubic colorless crystals, soluble in chloroform, ethanol, benzene and toluene. The solution IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **2b** and **2a** were identical.

### X-ray structure analysis of **2b**

Colorless crystals (0.46 × 0.42 × 0.18 mm<sup>3</sup>). Cell parameters: monoclinic,  $a = 1066.12(3)$ ,  $b = 2005.27(5)$ ,  $c = 1430.33(3)$  pm,  $\beta = 103.437(1)^\circ$ ,  $V = 2974.1(1) \times 10^6$  pm<sup>3</sup>, space group  $P2_1/n$  ( $Z = 2$ ),  $d_{\text{calc}} = 1.583$  g/cm<sup>-3</sup>.

Data collection. The crystals were mounted on a Siemens SMART diffractometer (area detector) and measured in a nitrogen stream. Mo K $\alpha$  radiation ( $\lambda = 71.069$  pm, graphite monochromator) was used for all measurements. The cell dimensions were refined with all unique reflections. The data collection at 233 K covered a hemisphere of the reciprocal space, by a combination of three sets of exposures. Each set had a different  $\phi$  angle for the crystal, and each exposure took 20s and covered 0.3° in  $\omega$ . The collected data range was  $3.56 \leq 2\theta \leq 41.66^\circ$  (99.6% complete,  $R_{\text{int}} = 0.020$ ). The crystal-to-detector distance was 4.40 cm. 3114 unique reflections were obtained after correction for polarization and Lorentz effects ( $\mu = 7.61$  cm<sup>-1</sup>) and an empirical absorption correction (SADABS).

The structure was solved by direct methods (SHELXS86). The positions of the hydrogen atoms were calculated according to an idealized geometry. Refinement was performed by the full-matrix least-squares method based on  $F^2$  (SHELXL93) with anisotropic thermal parameters for all non-hydrogen atoms. The parameters of the hydrogen atoms were refined with a riding model.  $R = 0.027$ ,  $R_w = 0.068$  for all reflections;  $w = 1/[\sigma^2(F_o^2) + (0.0278 P)^2 + 4.55 P]$  [ $P = (F_o^2 + 2F_c^2)/3$ ]. The largest residual electron density was 0.350 e<sup>-</sup> Å<sup>-3</sup>.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44-1223-336033; e-mail: tech-

ed@ccdc.cam.ac.uk) quoting the depository number CCDC 137083.

### Copolymerization of **2b** with methylmethacrylate

0.375 g of **2b** (0.26 mmol) was dissolved in 3.5 ml of benzene, and 1.46 g of methylmethacrylate (14.5 mmol) were added. After addition of 0.02 g of benzoyl peroxide as radical starter, the mixture was stirred at 60 °C for 1 day. After removal of the solvent in vacuo, the polymer was washed twice with ethyl acetate in order to remove residual benzene and dried in vacuo for 12 h. A white solid was obtained. Elemental analysis (the theoretical values refer to complete incorporation of both methylmethacrylate and **2b**). Found: C, 54.11; H, 7.01. Calc.: C, 56.23; H, 7.26%.

Copolymerization with other **2b**/methylmethacrylate ratios was performed by the same procedure.

*1:100 ratio:* 0.488 g (0.34 mmol) of **2b** in 5 ml of benzene, 3.44 g of methylmethacrylate (34.3 mmol), 0.027 g benzoyl peroxide. A slightly opaque glass was obtained. Elemental analysis. Found: C, 58.86; H, 7.66. Calc.: C, 57.69; H, 7.57%.

*1:207 ratio:* 0.432 g (0.31 mmol) of **2b** in 11 ml of benzene, 6.23 g of methylmethacrylate (62.2 mmol), 0.05 g of benzoyl peroxide. A hard, elastic yellowish polymer was obtained. Elemental

analysis. Found: C, 58.12; H, 7.75. Calc.: C, 58.79; H, 7.78%.

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