Macromol. Symp. ***175,*** *357–366 (2001)*

Cross-Linking of Poly(methyl methacrylate) by Oxozirconate and Oxotitanate Clusters

Gregor Trimmel,[a] *Bogdan Moraru,*[a] *Silvia Gross,*[b] *Vito Di Noto,*[b]
Ulrich Schubert[a]*

[a] Institut für Anorganische Chemie, Technische Universität Wien, Getreidemarkt 9, A-1060 Wien, Austria

[b] Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università degli Studi di Padova, via Loredan, I-35131 Padova, Italy

SUMMARY: Radical polymerization of methyl methacrylate with 0.5 - 2 mol% of the (meth)acrylate-substituted oxozirconium and oxotitanium clusters $Zr_6(OH)_4O_4(OMc)_{12}$ (OMc = methacrylate), $Zr_4O_2(OMc)_{12}$, $Ti_6O_4(OEt)_8(OMc)_8$ and $Ti_4O_2(OPr^i)_6(OAcr)_6$ (OAcr = acrylate) results in an efficient cross-linking of the organic polymers. The obtained inorganic-organic hybrid polymers exhibit a higher thermal stability due to inhibited depolymerization reactions. Contrary to undoped poly(methyl methacrylate), the cluster cross-linked polymers are insoluble but swell in organic solvents. The solvent uptake upon swelling decreases with an increasing amount of polymerized cluster. The impedance spectra of PMMA doped with various proportions of $Zr_4O_2(OMc)_{12}$ show that the capacitance of the polymers decreases with an increasing proportion of the cluster. The polymer doped with 2 mol% of $Zr_4O_2(OMc)_{12}$ shows an increase in conductivity to $0.9 \cdot 10^{-7}$ $S \cdot cm^{-1}$ at 74 °C.

Introduction

The so-called POSS-reinforced polymers (POSS = polyhedral oligomeric silsesquioxanes) have gained much interest as a new class of inorganic-organic hybrid material. They are characterized by the covalent incorporation of structurally well-defined organosilicate clusters in organic polymers, and are prepared by copolymerization of organic monomers with mainly the cubic $R_8Si_8O_{12}$ clusters, in which one [1] or more [2] of the organic substituents R contains a polymerizable group.

In addition to the properties observed for the POSS-systems, the reinforcement of organic polymers by covalently bonded, structurally well-defined oxometallate clusters, especially those of transition metals, could allow interesting modifications of the optical properties of the polymers, and the preparation of polymers with special magnetic or catalytic properties.

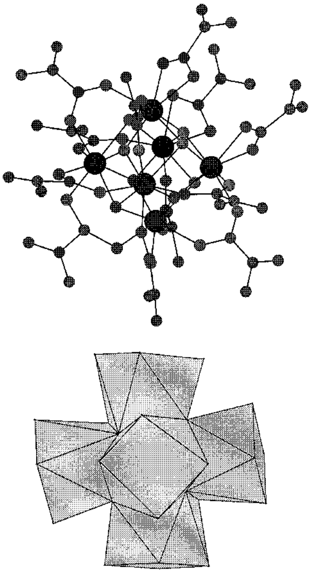
© WILEY-VCH Verlag GmbH, D-69469 Weinheim, 2001 CCC 1022-1360/00/$ 17.50+.50/0

Previously only a few oxometallate clusters substituted with polymerizable organic groups and incorporated into organic polymers by covalent bonding were known. Copolymerization of $Bu_{12}Sn_{12}O_{14}(OH)_6(OMc)_2$ (Bu = butyl, OMc = methacrylate) with methyl methacrylate achieved only low levels of cross-linking. The stannate clusters acted mainly as terminating units [3]. Polystyrene foams were produced by copolymerization of styrene with $Ti_3O_2(OPr^i)_5(OCMe{=}CH_2)_3(Pr^iOH)$ [4]. The methacrylate-substituted heteropolyanion $[SiW_{10}O_{36}(Si_2R_2O)]^{4-}$ (R = $(CH_2)_3OC(O)CMe{=}CH_2$) was copolymerized with ethyl methacrylate [5].

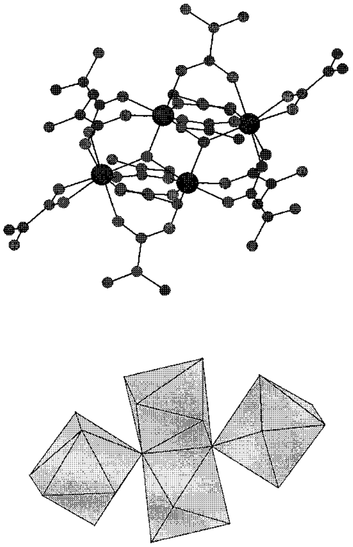
Over the past few years we have isolated several acrylate- or methacrylate-substituted oxotitanate, oxozirconate and mixed oxotitanate/oxozirconate clusters of differing size and shape [6-12]. In each case, the cluster core is surrounded by the organic ligands. The crystalline clusters are reproducibly obtained in very high yields by reacting $Zr(OR)_4$ or $Ti(OR)_4$ with a defined excess of (meth)acrylic acid. In the first step of this reaction, one or more alkoxide ligands are substituted by carboxylate groups. The thus liberated alcohol then undergoes an esterification reaction. The water produced together with the ester serves to hydrolyze the remaining alkoxide groups and acts as the source of the oxide or hydroxide groups in the clusters. The very slow production of water allows a very controlled growth of the carboxylate-substituted oxometallate clusters.

The molecular structures of the clusters discussed in this article, $Zr_6(OH)_4O_4(OMc)_{12}$ (**1**), $Zr_4O_2(OMc)_{12}$ (**2**), $Ti_6O_4(OEt)_8(OMc)_8$ (**3**) and $Ti_4O_2(OPr^i)_6(OAcr)_6$ (**4**), are shown in Fig. 1. The plots below the ball-and stick models show the linkage of the coordination polyhedra (only the metal and oxygen atoms are shown in these representations) and that the double bonds of the (meth)acrylate ligands are fully accessible for chemical reactions.

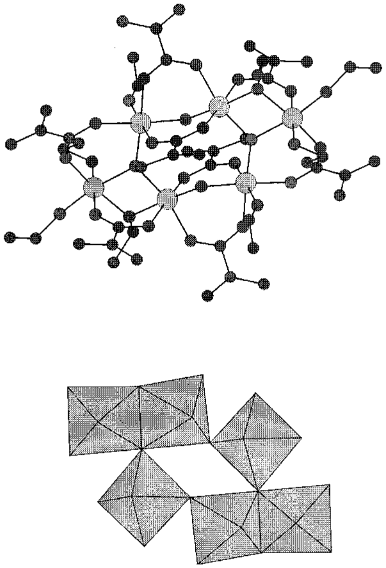
The copolymerization of various portions of the clusters **1** - **4** with methyl methacrylate (r_c = olefin / cluster molar ratio) [12] and some of the properties of the thus obtained cluster-reinforced poly(methyl methacrylate) (PMMA) are discussed in this article. Preliminary reports on the incorporation of the oxotitanium and oxozirconium clusters in PMMA and poly(methacrylic acid) have been published [8, 13]. The results show that the polymer is very efficiently crosslinked by the clusters and that the properties of the cluster cross-linked materials depend on the proportion of the incorporated cluster. It should be noted that PMMA copolymerized with 1 mol% of the clusters (r_c = 100) contains 6.2 and 4.2 wt% of ZrO_2 when doped with **1** or **2**, respectively, and 4.2 and 2.9wt% of TiO_2 when doped with **3** or **4**.



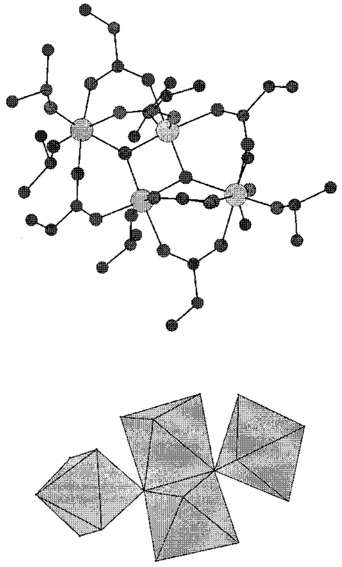
$Zr_6O_4(OH)_4(OMc)_{12}$ (**1**)



$Zr_4O_2(OMc)_{12}$ (**2**)



$Ti_6O_4(OEt)_8(OMc)_8$ (**3**)



$Ti_4O_2(OPr^i)_6(OAcr)_6$ (**4**)

Fig. 1: The molecular structures of the clusters employed for the cross-linking of PMMA.

Results and Discussion

Preparation and appearance of the hybrid polymers

Radical-initiated polymerization of **1** - **4** with a 50- to 1000-fold molar excess of methyl methacrylate, in benzene or toluene at 65°C with dibenzoylperoxide as the initiator, gave hybrid polymers which still contained some solvent after drying at reduced pressure [14]. Residual solvent was removed by extraction with ethyl acetate. The appearance of the polymers after removal of the solvent depends on the cluster type and the amount of incorporated cluster. The polymers doped by the zirconate clusters **1** or **2** were colorless; low cluster proportions ($r_c > 100$) lead to transparent glassy polymers, while opaque glasses to white solids were obtained with higher cluster proportions ($r_c \approx 50$). Doping by the titanate clusters **3** or **4** resulted in yellowish, transparent glasses. The reason for the different appearance is currently unknown; it could be due to a different degree of direct cross-linking between the clusters, which could increase with a higher the cluster content.

The ^{13}C MAS NMR spectra of the polymers cross-linked by the clusters **1** - **3** (r_c between 50 and 200; polymers crosslinked with **4** were not yet investigated by NMR) show very weak signals corresponding to unreacted methacrylate ligands of the clusters. Although the spectra indicate that the majority of the cluster-bonded methacrylate ligands underwent polymerization reactions, the signals do not allow quantification the proportion of unreacted methacrylate units.

Small-angle scattering (SAXS) experiments on PMMA samples cross-linked by the clusters **1** - **3** showed that the clusters are incorporated into the polymers in a random orientation [8,13]. The radius of gyration of the clusters corresponds very well to the cluster radius determined by X-ray crystallography. Although the SAXS data show that the microstructure of all cluster-doped samples can be described by a dispersion of identical spherical or disk-shaped clusters in the polymer, the increase of the spacing between the clusters, however, is much less than would be expected from the dilution. Therefore, some agglomeration of the clusters (i.e., the onset of a microphase separation) can be considered.

The clusters **1** – **4** are moisture sensitive. Nevertheless, the cluster cross-linked polymers are even stable at ambient atmosphere for prolonged periods, and their properties do not change. Particularly the glassy, transparent polymers do not get turbid. This indicates that the clusters are either protected against hydrolysis once incorporated into the polymer, or do not form larger zirconia or titania particles after hydrolysis.

Swelling behavior

While undoped poly(methyl methacrylate) (PMMA) dissolves in various organic solvents, the cluster cross-linked polymers only swell. The solvent uptake per gram of the polymer within 3 d is shown in Fig. 2. The swelling behavior of the cluster-reinforced PMMA in ethyl acetate shows a clear dependence on the methyl methacrylate / cluster molar ratio (r_c). This relationship clearly shows that the cross-linking density increases with an increasing proportion of the cluster. Interestingly, the swelling of the polymers depends on the type of incorporated cluster. The zirconate cross-linked PMMA swells less when **2** is the cluster component. The cross-linking efficiency of **2** therefore appears to be somewhat higher than that of **1**, possibly due to the more open and flatter structure of **2**. The difference between the polymers doped with **3** or **4** is more pronounced. Cluster **4** has a rather low cross-linking efficiency. This behavior could be due to the smaller number of acrylate ligands and possibly their spatial distribution.

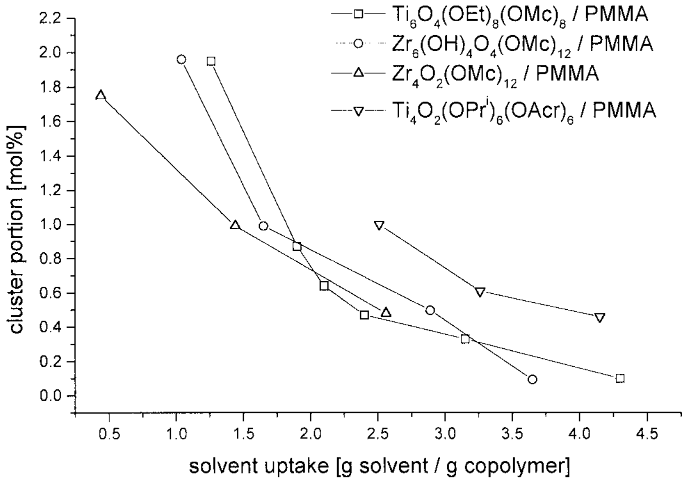


Fig. 2: Swelling behavior of the cluster cross-linked PMMA (a cluster portion of 1% corresponds to $r_c = 100$, etc). The polymers were stored in ethyl acetate for 3 d.

Thermal degradation

Undoped PMMA decomposes above 330 °C by depolymerization reactions. The onset of the thermal decomposition of the cluster-doped polymers is slightly shifted to higher temperatures compared with the undoped polymers. Fig. 3 shows the DSC curves of PMMA, and

PMMA reinforced by different ratios of cluster **1**; the general thermal behavior of PMMA cross-linked by the clusters **2** or **3** is the same.

Compared with undoped PMMA, thermal depolymerization is distinctly less pronounced for the polymers with $r_c = 100$ and 200, and disappears for the polymer with $r_c = 50$. At higher temperatures the polymers are oxidatively degraded (the experiments were performed in air). The mass of the solid residues in the TGA experiments upon heating the polymers to 800°C corresponds very well to the ZrO_2 or TiO_2 content.

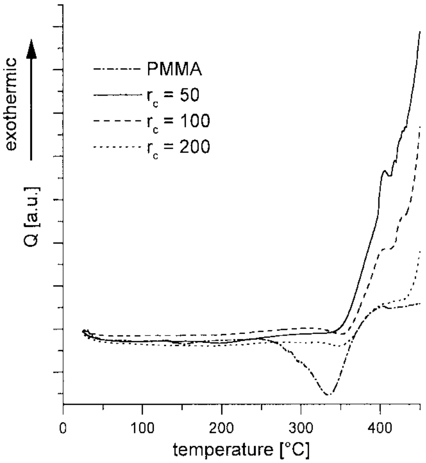


Fig. 3: Differential scanning calorimetry (in air). undoped PMMA and the polymers cross-linked by cluster **1**.

Electric properties

The electrical properties of the new hybrid polymers were tested by measuring the impedance as a function of the frequency, the temperature and their composition [16]. Impedance spectra were recorded in the frequency range 20 Hz - 1 MHz, at 18.8 °C and 74 °C. As an example, Fig. 4 shows the spectrum of the polymer containing 2 mol% of **2** ($r_c = 50$). A semicircular profile intersecting the origin is typical for a system characterized by the presence of a resistance in parallel with a capacitance. The rise of the temperature from 18.8 °C to 74 °C results in a bending of the profile towards the abscissa, thus indicating that at $T > 70$ °C the conductivity of the hybrid polymer is $0.9 \cdot 10^{-6}$ $S \cdot cm^{-1}$. Analysis of the impedance spectra of samples, with a $r_c = 100$ or 200, shows a linear correlation between r_c and the dielectricity of the material: the higher r_c the more dielectric is the material. These results clearly show that:

- the electrical properties of the investigated hybrids materials are tunable by the proportion of the cluster incorporated into the polymer. When the cluster proportion is lowered, the dielectric level of the material is getting closer to that of undoped PMMA.
- the mobility of the inorganic cluster inside the material is negligible.

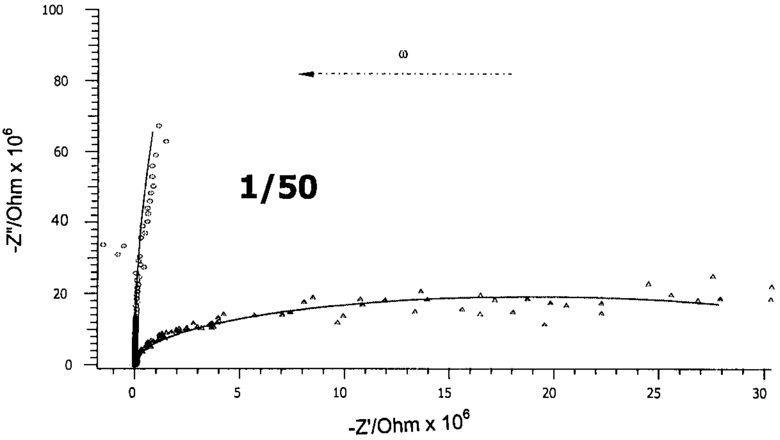


Fig. 4: Impedance spectrum of PMMA doped with cluster **2** (r_c = 50). The spheres represent the values at 18.8 °C, and the triangles the values at 74 °C.

In order to investigate in detail the electrical properties of the organic-inorganic hybrids, the measured spectra were simulated through NLLQ (non-linear least squares method) by using a model circuit consisting of a resistance in parallel with a constant-phase element. The n-value of the constant-phase element for all samples (PMMA doped with **2**, r_c ranging from 50 to 200) has a value close to one, thus indicating that this element corresponds to a pure capacitance. The resistance of the hybrid polymers with r_c = 100 and 200 turned out to be very high, thus confirming that these materials are excellent dielectrics. Both conductivity and capacitance of the samples are plotted as a function of the Zr/MMA molar ratio (Fig. 5). A noticable effect of the temperature on the conductivity can only be observed for the sample with r_c = 50. For the samples with r_c = 100 and 200 this effect is not observed, due to their high dielectricity. These results are confirmed by the observation that the capacitance of the system increases when the methylmethacrylate proportion in the hybrid polymers is increased. On account of these findings, it can be suggested that as the proportion of PMMA in the material increases, the concentration of zirconium-based charge carriers is reduced and the system becomes more and more similar to a dielectric material like pristine PMMA.

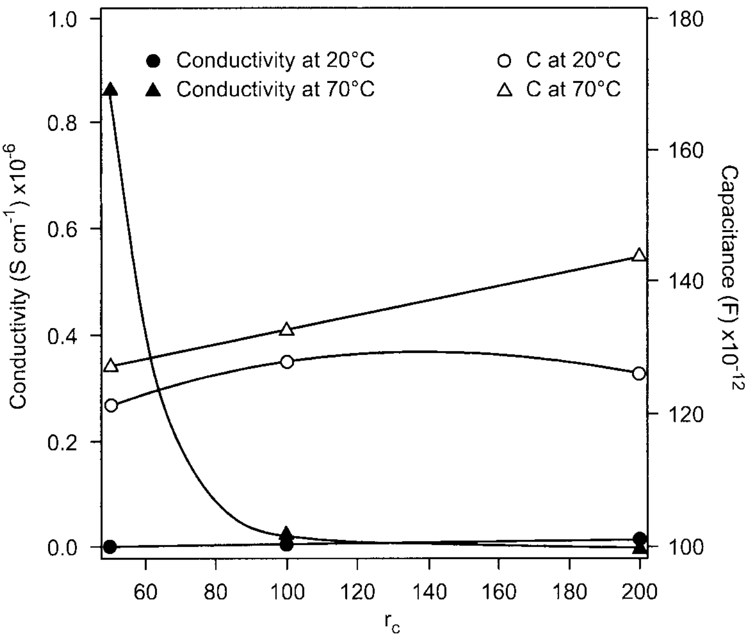


Fig. 5: Conductivity and capacitance of PMMA doped with cluster **2** in dependence of r_c.

Conclusions

Inorganic-organic hybrid polymers with zirconium or titanium oxide components were previously made from $Zr(OR)_4$ or $Ti(OR)_4$ precursors modified by polymerizable organic ligands [14], or by copolymerization of zirconyl acrylates and acrylic esters [15]. 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 based on structurally well-defined clusters which can be considered monodispersed nanoparticles. We have shown that copolymerization of the oxozirconium and oxotitanium clusters **1** - **4** with methacrylic acid or methyl methacrylate results in materials in which clusters cross-link the polymer chains via their surface-bonded organic groups. Owing to the large number of (meth)acrylate ligands, the cluster cross-linking the polymer chains occurs very efficiently even when only a small molar percentage of the clusters is employed.

The preparation of the inorganic-organic polymers described in this article is basically a two-step process. In the first step, the oxo clusters are prepared by carefully controlled hydrolysis of methacrylate-substituted $Zr(OR)_4$ or $Ti(OR)_4$. The isolated clusters are then copolymerized with olefins. The thus obtained hybrid polymers are doped with covalently bonded uniform metal oxide nanoparticles.

Apart from the thermal, dielectric and swelling properties described in this article, the hybrid polymers are expected to have interesting mechanical and optical properties. An investigation of these properties is in progress. A gradual modification of the properties of the hybrid polymers is possible: (i) by modifying the monomer : cluster ratio, (ii) by modifying the cluster size, or (iii) by changing the metal.

Acknowledgements

This work was financially supported by the Fonds zur Förderung der wissenschaftlichen Forschung (FWF), Austria.

References

1. For example: T. S. Haddad, J. D. Lichtenhan, *Macromolecules*, **29**, 7302 (1996). J. J. Schwab, J. D. Lichtenhan, K. P. Chaffee, P. T. Mather, A. Romo-Uribe, *Mat. Res. Soc. Symp. Proc.*, **519**, 21 (1998). J. D. Lichtenhan, T. S. Haddad, J. J. Schwab, M. J. Karr, K. P. Chaffee, P. T. Mather, *Polym. Prep.*, **39(1)**, 489 (1998). J. Pynn, K. Matyjaszewski, *Macromolecules*, **33**, 217 (2000).
2. For example: A. Sellinger, R. M. Laine, *Macromolecules*, **29**, 2327 (1996). E. K. Lin, C.-R. Snyder, F. I. Mopsik, W. E. Wallace, W. L. Wu, C. X. Zhang, R. M. Laine, *Mat. Res. Soc. Symp. Proc.*, **519**, 15 (1998).
3. F. Ribot, F. Banse, C. Sanchez, M. Lahcini, B. Jousseaumme, *J. Sol-Gel Sci. Technol.*, **8**, 529 (1997). L. Angiolini, D. Caretti, C. Carlini, R. De Vito, F. T. Niesel, E. Salatelli, F. Ribot, C. Sanchez, *J. Inorg. Organomet. Polym.*, **7**, 151 (1998).

4. L. G. Hubert-Pfalzgraf, N. Pajot, R. Papiernik, S. Parraud, *Mat. Res. Soc. Symp. Proc.*, **435**, 137 (1996).
5. C. R. Mayer, R. Thouvenot, T. Lalot, *Chem.Mater.*, **12**, 257 (2000).
6. G. Kickelbick, U. Schubert, *Mat. Res. Soc. Symp. Proc.*, **519**, 401 (1998).
7. G. Kickelbick, U. Schubert, *Chem.Ber.*, **130**, 473 (1997).
8. G. Trimmel, S. Gross, G. Kickelbick, U. Schubert, *Appl. Organomet. Chem.*, in press.
9. G. Kickelbick, P. Wiede, U. Schubert, *Inorg. Chim. Acta*, **284**, 1 (1999).
10. U. Schubert, E. Arpac, W. Glaubitt, A. Helmerich, C. Chau, *Chem.Mater.* **4**, 291 (1992).
11. G. Kickelbick, U. Schubert, *Europ. J. Inorg. Chem.* 159 (1998).
12. A typical procedure is as follows: To a solution of 2.62 g (26.2 mmol) methyl methacrylate (filtered over alumina to remove the stabilizer) and 0.91 g (0.54 mmol) of **1** in 6 ml benzene, 21 mg (0.09 mmol) of dibenzoylperoxide were added. 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 olefin : initiator : solvent ratio was kept constant when the cluster: olefin ratio was varied.
13. G. Trimmel, P. Fratzl, U. Schubert, *Chem.Mater.* **12**, 602 (2000).
14. S. Besecke, G. Schröder, W. Gänzler, *German patent* DE 31 37 840 C2 (1981).
15. R. Di Maggio, L. Fambri, A. Guerriero, *Chem. Mater.*, **10**, 1777 (1998). C. Sanchez, M. In, *J. Non-Cryst. Solids*, **147&148**, 1 (1992). M. In, C. Gerardin, J. Lambard, C. Sanchez, *J. Sol-Gel Sci. Technol.*, **5**, 101 (1995). M. Camail, M. Humbert, A. Margaillan, J. L. Vernet, *Polymer*, **39**, 6533 (1998). H. T. Neher, W. R. Conn, E. H. Kroeker, *US patent* US 2,502,411 (1947).
16. V. Di Noto, D. Barreca, C. Furlan, L. Armelao, *Polym. Adv. Technol.* **11**, 108 (2000).