

Hybrid Organic/Inorganic Epoxy Resins Prepared by Frontal Polymerization

SERGIO SCOGNAMILLO, VALERIA ALZARI, DANIELE NUVOLI, ALBERTO MARIANI

Dipartimento di Chimica, Università di Sassari, and local INSTM Unit, Via Vienna 2, 07100 Sassari, Italy

Received 9 April 2010; accepted 23 July 2010

DOI: 10.1002/pola.24263

Published online 7 September 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The syntheses of hybrid epoxy resins made from different ratios among bisphenol-A diglycidyl ether, 3-glycidoxypropyltrimethoxysilane (GPTMS), and diethylenetriamine were successfully performed by using frontal polymerization. Conversions were always almost quantitative, and, because of the use of this alternative convenient technique, materials were prepared in very short times. Samples were characterized by DSC, TGA, IR spectroscopy, and solvent extraction. It was found that those materials containing a relatively high-Si

amount exhibit two different transition temperatures, with the highest one that increases as the content of GPTMS raises. The analogies and the differences with the analogous samples prepared by the classical batch technique are discussed. © 2010 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 48: 4721–4725, 2010

KEYWORDS: curing of polymers; epoxy resins; frontal polymerization; glass transition; thermosets

INTRODUCTION Epoxy resins are extensively used in many practical applications mostly because of their good mechanical properties.¹ On this respect, the addition of inorganic components to obtain hybrid materials² can be a useful way for further improving their characteristics. Indeed, they exhibit the advantages of both the organic polymers (flexibility, toughness, etc.) and the inorganic ones (high-heat resistance, good mechanical and optical properties).³ Thus, by combining the appropriate organic and inorganic starting moieties, a wide family of hybrid polymers to be used in an increased number of applications has been synthesized.^{2,4}

An important class of organic–inorganic epoxy materials is represented by 3-glycidoxypropyltrimethoxysilane (GPTMS)-derived hybrids.⁵ In particular, Ochi et al.^{6,7} investigated the silica/epoxy hybrids prepared from bisphenol-A diglycidyl ether (DGEBA) and GPTMS.

Frontal polymerization (FP) is a technique that allows the fast conversion of a monomer into a polymer by means of the exothermicity of the polymerization reaction itself. The released heat generates a polymerization front able to self-sustain and propagate along the whole reactor without further energy supply. A large number of systems have been investigated, namely acrylic monomers,^{8–11} glycidyl ethers,¹² polyurethanes,^{13,14} and interpenetrating polymer networks.¹⁵ Recently, FP was also applied to obtain controlled drug release systems,¹⁶ thermoresponsive,^{17,18} and super water absorbent hydrogels.¹⁹

Frontal curing of epoxy systems were studied by White et al.^{20,21} and by our group.^{22–25} Moreover, Chen and coworkers obtained epoxy resins/polyurethane networks,²⁶

Chekanov et al.²⁷ studied their mechanical and thermal properties, whereas Pojman and coworkers focused their attention on the obtainment of epoxy resins in the presence of BX₃-amine complexes as curing agents.^{28,29}

In this study, FP was exploited as a convenient method for the modification of the well-known DGEBA/diethylenetriamine (DETA)⁷ epoxy resin with various amounts of GPTMS (Fig. 1).

The influence of the ratio among all components on the front velocity (V_f) and its maximum temperature (T_{max}) and on the thermal properties of the obtained materials was studied.

EXPERIMENTAL

Materials

Bisphenol-A diglycidyl ether (DGEBA, FW = 340.4, mp = 40–44 °C, d = 1.16 g/mL), DETA (FW = 103.2, bp = 199–209 °C, d = 0.95 g/mL), and 3-glycidoxypropyl trimethoxy silane [GPTMS, FW = 236.3, bp = 120 °C (2 mm Hg), d = 1.07 g/mL] were purchased from Sigma-Aldrich and used as received. At 25 °C, all the starting mixtures discussed below were characterized by pot-lives longer than 6 h.

Characterization

DSC thermal characterization was performed by means of a Q100 Waters TA Instruments calorimeter, with a TA Universal Analysis 2000 software. DSC investigations were carried out under dry argon atmosphere, from –80 to 250 °C, with a heating rate of 10 °C/min. For each sample, two thermal

Correspondence to: A. Mariani (E-mail: mariani@uniss.it)

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 48, 4721–4725 (2010) © 2010 Wiley Periodicals, Inc.

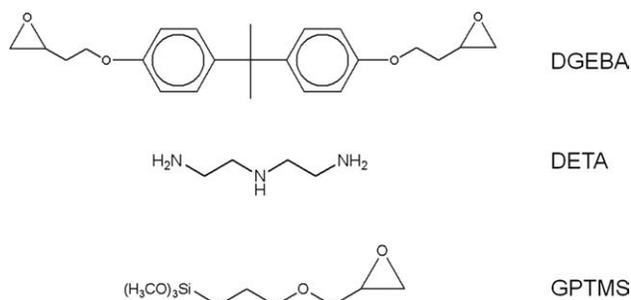


FIGURE 1 Starting materials used in this work.

scans were collected in the aforementioned temperature range; the first scan was performed to fully convert possible residual reactants; the second was done to determine glass transition temperatures (T_g).

A Fourier transform infrared spectroscope (JASCO FT 480 spectrometer) was used for recording the FTIR spectra of the samples. The powders were ground into a dry KBr disk, and 32 scans at a resolution of 4 cm^{-1} were used to record the spectra.

TGA measurements were performed using a TA Instrument thermobalance, TGA 2050, under air flow, from 25 to $800\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$.

Synthesis of Hybrid Polymers

FP Runs

A common transparent glass test tube (i.d. = 1.5 cm, length = 16 cm) was filled with the appropriate amounts of DGEBA, DETA, and GPTMS. To remove any bubble inside the viscous liquid, the starting mixtures were sonicated in an ultrasound bath at $25\text{ }^\circ\text{C}$ for 30 s. A thermocouple junction was placed at about 1 cm from the bottom of the tube and connected to a digital temperature recorder. The polymerization front was generated by heating the external wall of the tube in correspondence with the upper surface of the monomer mixture; then the position of the front against time was measured. Front temperature measurements were monitored by using a K-type thermocouple connected to a digital thermometer (Delta Ohm 9416) used for temperature reading and recording (sampling rate: 1 Hz). For all samples, front temperature ($\pm 10\text{ }^\circ\text{C}$) and front velocity ($\pm 0.05\text{ cm}/\text{min}$) were measured. The obtained polymers were purified by soxhlet extraction with CHCl_3 for 72 h, and the residual monomer content was determined by measuring the weight decrease. Polymer yields, determined by DSC,²⁴ were always almost quantitative (residual polymerization heat detected during the first scan was negligible).

Batch Runs

A series of specimens having the same composition as those prepared by FP was synthesized by the classical method³⁰ in a batch reactor immersed in a thermostated oil bath set at $60\text{ }^\circ\text{C}$. The reactions were carried out for 2 h and, after cooling, the samples underwent the same purification procedure described earlier. Also, in this case, polymer yields were almost quantitative.

RESULTS AND DISCUSSION

To get hybrid organic/inorganic epoxy resins containing DGEBA, GPTMS, and DETA, some preliminary investigations were carried out, thus determining the ratio ranges among the components that allow the front to self-sustain.

Initially, some experiments were performed by keeping the ratio between the number of primary amine groups and that of the epoxy ones (which were the sum of those coming from DGEBA and GPTMS) equal to 1:2. In particular, two different ratios between DGEBA and GPTMS were tested. The first was characterized by a molar amount of GPTMS equal to 2.5% of that of DGEBA; in the second, this ratio was raised to 25%.

In both runs, front did not self-sustain as a consequence of the occurrence of fingering. This phenomenon occurs when a polymer is denser than the corresponding monomer and melts at the front temperature; it is revealed by descending drops of hot polymer material that contaminate the lower zones of unreacted monomer, resulting in heat removal from the front.³¹

Then, some FP runs with a constant amount of DETA, by varying the relative amounts of DGEBA and GPTMS, were also performed. Namely, the following [DGEBA]/[GPTMS] were investigated: 3:1, 1:1, 1:3, and 0:1 mol/mol. Actually, FP was only observed when the ratio 3:1 was used; in this run, $T_{\text{max}} = 216\text{ }^\circ\text{C}$ and $V_f = 0.8\text{ cm}/\text{min}$ were found. In all the other cases, front did not self-sustain probably because of (i) the large amount of monofunctional reactant (GPTMS), which resulted in oligomer formation, not fully crosslinked; (ii) the increased content of non reacting material (i.e., the Si containing moiety), which resulted in an excessive amount of dissipated heat.

On this basis, in the next series, the ratio [GPTMS]/[DGEBA] was varied from 0 to 1.0 mol/mol, while the amount of crosslinker DETA was always kept equimolar to that of DGEBA. In Figure 2, T_{max} and V_f values referring to this series are displayed.

Although no significant variation of front temperature was observed in the whole range [GPTMS]/[DGEBA] = 0–1.0 mol/mol (T_{max} was always around $230\text{ }^\circ\text{C}$), with the minor exception of sample FP5, front velocity decreased as the amount of GPTMS increased. In fact, it went from $0.9\text{ cm}/\text{min}$, for the sample without GPTMS (FP1), to $0.6\text{ cm}/\text{min}$ for sample FP9 ([GPTMS]/[DGEBA] = 1.0 mol/mol).

It should be underlined that these front velocities allow one to cure thick materials in times that are much shorter than those typically required by the classical methods (just a few minutes instead of a few hours).

To evaluate the conversion and the glass transition temperature of the obtained hybrid materials, DSC analyses were performed (not shown). The negligible residual polymerization heat recorded during the first scans indicates that conversions were always almost quantitative.

Table 1 lists the T_g values found for all samples of this series, obtained by both FP and classical batch polymerization

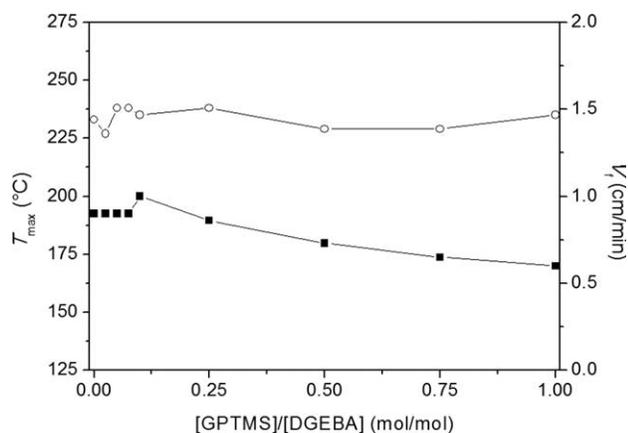


FIGURE 2 Front temperature T_{max} (○) and front velocity V_f (■) as functions of the molar amounts of GPTMS for samples FP1–9 ([DGEBA] = [DETA]).

(BP). As can be seen, when the ratio [GPTMS]/[DGEBA] becomes relatively large, the obtained materials exhibit two T_g values. It seems reasonable to attribute the lowest transition to the fully organic polymer portions, which are characterized by relatively high mobility, and the highest to partial Si–O–Si crosslinking.³²

However, some differences were found between FP and BP samples. Namely, while for the latter, the appearance of two transition temperatures was found for all the GPTMS-containing samples, for the frontally polymerized ones, this was found only for those obtained from [GPTMS]/[DGEBA] ≥ 0.10 mol/mol. In particular, the lowest value is always comprised between 45 and 73 °C for the BP samples, and between 50 and 70 °C for the FP ones.

The different behavior derived by the two polymerization techniques can be explained as follows: as already reported in refs. 33 and 34, FP materials retain some of the characteristics of the starting monomer mixture more than what the BP ones do. This is due to the fast-conversion process that characterizes FP, which may “freeze” the components in a metastable polymeric phase. In the present case, for [GPTMS]/[DGEBA] ≤ 0.1 mol/mol (FP1–4), the clustering of

the silyl groups is avoided or occurs in negligible extent; consequently, only one glass transition temperature is exhibited, which is higher than that of the sample FP1, which does not contain GPTMS at all. As the amount of GPTMS increases, the effect of the polymerization technique becomes not sufficient to avoid this possible molecular segregation, and the two T_g s become evident also in the case of the FP materials (FP5–FP9).

As far as the highest T_g value is concerned, this is located at values ranging from 65 and 108 °C for the BP samples, while it is higher for the materials prepared by FP, that is, from 74 and 150 °C. This difference is again in agreement with the higher degree of homogeneity that characterizes the materials prepared by FP. Indeed, one may suppose that, for relatively large contents of Si-containing moieties, the inorganic parts are more homogeneously dispersed as a consequence of the FP process, thus resulting in a material characterized by a general network mobility reduction.³⁵

The aforementioned presence of a Si–O–Si crosslinking and the complete monomer conversion can be detected by FTIR analysis.^{36,37} The infrared spectra of all the DGEBA/DETA/GPTMS hybrid polymers synthesized via FP (FP1–9) or BP (B1–B9) were very similar, thus suggesting that the polymerization technique does not significantly affect the molecular structure. For such a reason, for the sake of clarity only six, representative spectra are displayed in Figure 3. By comparing the spectra of the cured epoxy samples [FP1, FP7, and FP9 in Figure 3(a), and B1, B7 and B9 in Fig. 3(b)] with those of the starting materials [Fig. 3(c)], the complete disappearance of the characteristic epoxide group band at 916 cm^{-1} , and the appearance of a band at 1106 cm^{-1} (diagnostic for epoxy crosslinking) are evident, thus clearly indicating that the reactants underwent full conversion. Moreover, the simultaneous appearance of the broad bands at 3600–3100 cm^{-1} (ascribed to OH stretching), and at 1200–1000 cm^{-1} attributed to the Si–O–Si asymmetric stretching, indicate the presence of a silicon-oxide network inside the polymers.

TGA investigations were also carried out. Even in this case, for the sake of simplicity, in Figure 4, thermograms relating to the above six samples FP1, FP7, FP9 and B1, B7, and B9 are reported.

TABLE 1 T_g Values of Samples Obtained Via FP and BP for Various [GPTMS]/[DGEBA] ratios (in all cases, [DGEBA] = [DETA])

[GPTMS]/[DGEBA] (mol/mol)	FP Sample Code	T_g (°C)		BP Sample Code	T_g (°C)	
0	FP1	51		B1	62	
0.025	FP2	60		B2	50	65
0.050	FP3	63		B3	45	67
0.075	FP4	67		B4	49	67
0.10	FP5	58	77	B5	49	73
0.25	FP6	50	74	B6	54	86
0.50	FP7	59	86	B7	53	92
0.75	FP8	62	104	B8	61	91
1.0	FP9	70	150	B9	73	108

Actually, either the FP or batch hybrids made of the same reactant composition showed analogous trends. In detail, all the polymers showed $\sim 2\%$ weight decrease due to loss of the residual water, followed by decomposition at $T_{\text{onset}} \sim 300\text{--}350\text{ }^{\circ}\text{C}$. In particular, this happens at values that increase as the content of GPTMS increases. This is in agreement with the weight loss due to the formation of the Si—O—Si linkages and the simultaneous formation of volatile compounds. However, because this reaction occurs at temperatures that are higher than those found during the FP runs (i.e., $\sim 230\text{ }^{\circ}\text{C}$), the extent of such linkage formation during the FP is probably rel-

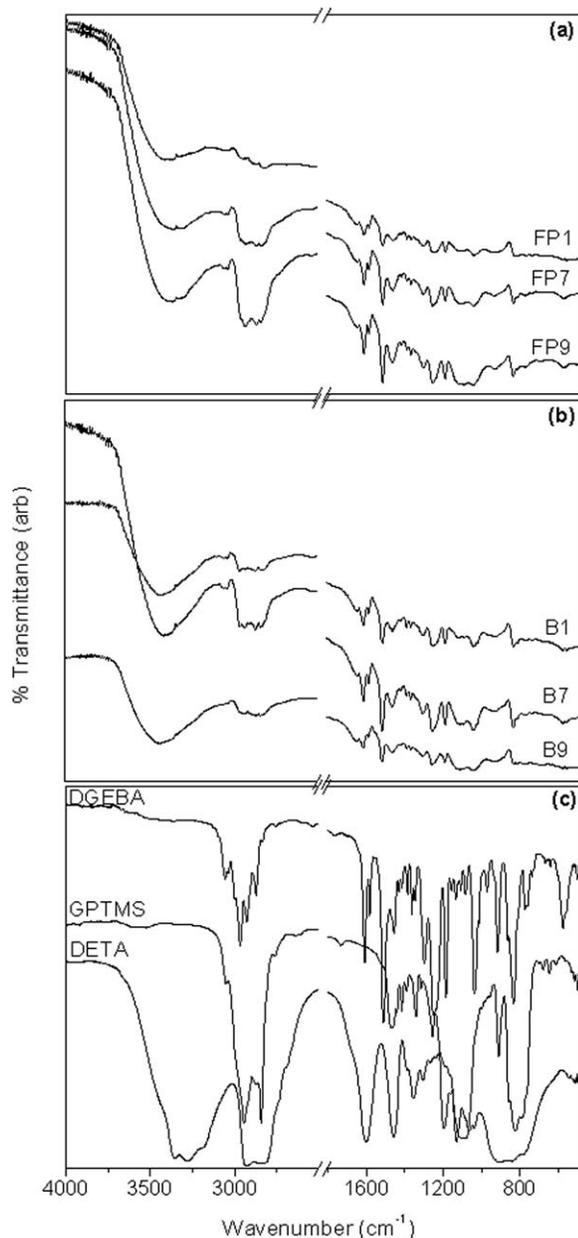


FIGURE 3 FTIR spectra; (a) hybrid polymers via FP, (b) hybrid polymers via BP, (c) DGEBA, DETA, and GPTMS (FP1 or B1, GPTMS = 0 mol %; FP7 or B7, [GPTMS]/[DGEBA] = 0.5 mol/mol; FP9 or B9 [GPTMS]/[DGEBA] = 1.0 mol/mol).

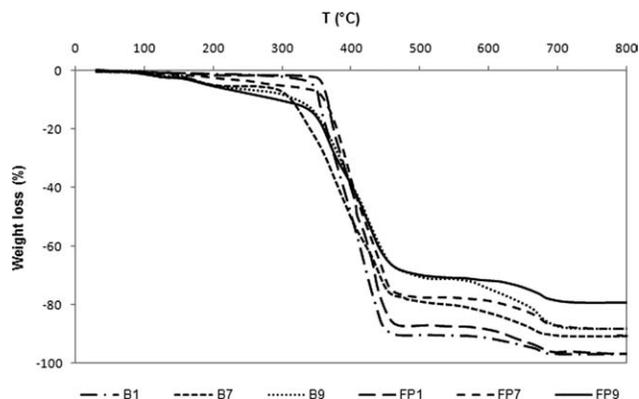


FIGURE 4 TGA traces for DGEBA/DETA/GPTMS hybrid polymers synthesized via FP or BP (FP1 or B1, GPTMS = 0 mol %; FP7 or B7, [GPTMS]/[DGEBA] = 0.5 mol/mol; FP9 or B9 [GPTMS]/[DGEBA] = 1.0 mol/mol).

ative little, thus allowing one to consider FP a reliable polymerization process for the present system.

CONCLUSIONS

For the first time, organic/inorganic epoxy resins were prepared by FP. The relative reactant ratio ranges that allows for the front to self-sustain have been determined. It was found that the molar ratio between DGEBA and DETA must be kept equal to 0.75–1. Despite it is a monofunctional reactant, GPTMS can be added to the reaction mixture without compromising conversion, which was always almost quantitative. It is also noteworthy that, for relatively large GPTMS contents, two different glass transition temperatures are observed, one always comprised between 50 and 70 $^{\circ}\text{C}$, probably due to the organic moiety only, and the second, at temperature up to 150 $^{\circ}\text{C}$ that may be attributed to the presence of the inorganic component. It is also noteworthy that the analogous batch samples show two different T_g values also for relatively low-GPTMS content, a phenomenon that may be attributed to a less homogeneous polymer structure; furthermore, for relatively large GPTMS contents, T_g does not exceed 108 $^{\circ}\text{C}$, thus indicating that the FP materials are characterized by minor mobility.

It should also be underlined that all runs were performed in times that are much shorter than those necessary for the corresponding batch samples (minutes instead of hours).

These results are in agreement with those obtained in many other FP studies, thus confirming the reliability of this technique.

S. Scognamiglio thanks “Regione Autonoma della Sardegna” for the financial support (“Master and Back” program).

REFERENCES AND NOTES

- May, C. A. In *Epoxy Resins: Chemistry and Technology*, 2nd ed.; May, C. A., Ed.; Marcel Dekker: New York, 1988.
- Mammeri, F.; Le Bourhis, E.; Rozesa, L.; Sanchez, C. J. *Mater Chem* 2005, 15, 3787–3811.

- 3** Sellinger, A.; Laine, R. M. *Chem Mater* 1996, 8, 1592–1593.
- 4** KICKELBICK, G. In *Hybrid Materials: Synthesis, Characterization, and Applications*; KICKELBICK, G., Ed.; Wiley-VCH: Weinheim, 2007; Chapter 1, p 1.
- 5** Yang, P.; Wang, G.; Xia, X.; Takezawa, Y.; Wang, H.; Yamada, S.; Du, Q.; Zhong, W. *Polymer Eng Sci* 2008, 48, 1214–1221.
- 6** Ochi, M.; Takahashi, R.; Terauchi, A. *Polymer* 2001, 42, 5151–5158.
- 7** Ochi, M.; Takahashi, R. *J Polym Sci Part B: Polym Phys* 2001, 39, 1071–1084.
- 8** Pojman, J. A. *J. Am Chem Soc* 1991, 113, 6284–6286.
- 9** Mariani, A.; Bidali, S.; Fiori, S.; Malucelli, G.; Ricco, L. *Macromol Symp* 2004, 218, 1–9.
- 10** Fang, Y.; Chen, L.; Chen, S. *J Polym Sci Part A: Polym Chem* 2009, 47, 1136–1147.
- 11** Nason, C.; Pojman, J. A. *J Polym Sci Part A: Polym Chem* 2008, 46, 8091–8096.
- 12** Crivello, J. V. *J Polym Sci Part A: Polym Chem* 2006, 44, 3036–3052.
- 13** Mariani, A.; Fiori, S.; Bidali, S.; Alzari, V.; Malucelli, G. *J Polym Sci Part A: Polym Chem* 2008, 46, 3344–3351.
- 14** Chen, S. U.; Sui, J.; Chen, L.; Pojman, J. A. *J Polym Sci Part A: Polym Chem* 2005, 43, 1670–1680.
- 15** Fiori, S.; Mariani, A.; Ricco, L.; Russo, S. *e-Polymers* 2002, 029, 1–10.
- 16** Gavini, E.; Mariani, A.; RASSU, G.; Bidali, S.; Spada, G.; Bonferoni, M. C.; Giunchedi, P. *Eur Polym J* 2009, 45, 690–699.
- 17** Caria, G.; Alzari, V.; Monticelli, O.; Nuvoli, D.; Kenny, J. M.; Mariani, A. *J Polym Sci Part A: Polym Chem* 2009, 47, 1422–1428.
- 18** Alzari, V.; Monticelli, O.; Nuvoli, D.; Kenny, J. M.; Mariani, A. *Biomacromolecules* 2009, 10, 2672–2677.
- 19** Scognamillo, S.; Alzari, V.; Nuvoli, D.; Mariani, A. *J Polym Sci Part A: Polym Chem* 2010, 48, 2486–2490.
- 20** White, S. R.; Kim, C. J. *Reinforced Plast Comp* 1993, 12, 520–535.
- 21** Kim, C.; Teng, H.; Tucker, C. L.; White, S. R. *J. Comp Mater* 1995, 29, 1222–1253.
- 22** Frulloni, E.; Salinas, M. M.; Torre, L.; Mariani, A.; Kenny, J. M. *J Appl Polym Sci* 2005, 96, 1756–1766.
- 23** Mariani, A.; Bidali, S.; Caria, G.; Monticelli, O.; Russo, S.; Kenny, J. M. *J Polym Sci Part A: Polym Chem* 2007, 45, 2204–2211.
- 24** Mariani, A.; Bidali, S.; Fiori, S.; Sangermano, M.; Malucelli, G.; Bongiovanni, R.; Priola, A. *J Polym Sci Part A: Polym Chem* 2004, 42, 2066–2072.
- 25** Mariani, A.; Alzari, V.; Monticelli, O.; Pojman, J. A.; Caria, G. *J Polym Sci Part A: Polym Chem* 2007, 45, 4514–4521.
- 26** Chen, S.; Tian, Y.; Chen, L.; Hu, T. *Chem Mater* 2006, 18, 2159–2163.
- 27** Chekanov, Y.; Arrington, D.; Brust, G.; Pojman, J. A. *J Appl Polym Sci* 1997, 66, 1209–1216.
- 28** Pojman, J. A.; Griffith, J.; Nichols, H. A. *e-Polymers* 2004, 13, 1–7.
- 29** Scognamillo, S.; Bounds, C.; Luger, M.; Mariani, A.; Pojman, J. A. *J Polym Sci Part A: Polym Chem* 2010, 48, 2000–2005.
- 30** Muhlfeld, A.; Schaubert, T.; Wagner, S.; (Carl Freudenberg KG, Weinheim (Germany)), Magna Eybl Systemtechnik GmbH, Straubing (Germany), U.S. Patent 6,573,341, June 3, 2003.
- 31** Pojman, J. A.; Craven, R.; Khan, A.; West, W. J. *Phys Chem* 1992, 96, 7466–7472.
- 32** Chan, C.-K.; Chu, I.-M. *Polymer* 2001, 42, 6823–6831.
- 33** Nagy, I. P.; Sike, L.; Pojman, J. A. *J Am Chem Soc* 1995, 117, 3611–3612.
- 34** Tredici, A.; Pecchini, R.; Sliepcevich, A.; Morbidelli, M. *J Appl Polym Sci* 1998, 70, 2695–2702.
- 35** Girard-Reydet, E.; Lam, T. M.; Pascault, J. P. *Macromol Chem Phys* 1994, 195, 149–158.
- 36** Nikolic, G.; Zlatkovic, S.; Cakic, M.; Cakic, S.; Lacnjevac, C.; Rajic, Z. *Sensors* 2010, 10, 684–696.
- 37** Gizdavic-Nikolaidis, M. R.; Edmonds, N. R.; Bolt, C. J.; East-eal, A. J. *Curr Appl Phys* 2008, 8, 300–303.