

Polyaniline/Maleic Acid Copolymers Composites: Synthesis and Characterization

Mircea Grigoras,^{*1} Gabrielle-Charlotte Chitanu,¹ Irina Popescu,¹
Irina-Mihaela Pelin,¹ Gimi-Aurelian Rimbu²

Summary: Polyaniline/maleic acid copolymers composites were synthesized by chemical *in situ* polymerization of aniline using ammonium peroxodisulfate as oxidant, in the presence of water soluble copolymers containing carboxylic groups. Fine dispersions of composite materials, soluble in N,N-dimethylformamide or dimethyl sulfoxide were obtained which can be processed as thin films and membranes for application as proton-conductive materials for electrolyte membranes of fuel cells. The composites were characterized by FTIR spectroscopy and thermal methods.

Keywords: composites; maleic acid copolymers; polyaniline; template polymerization

Introduction

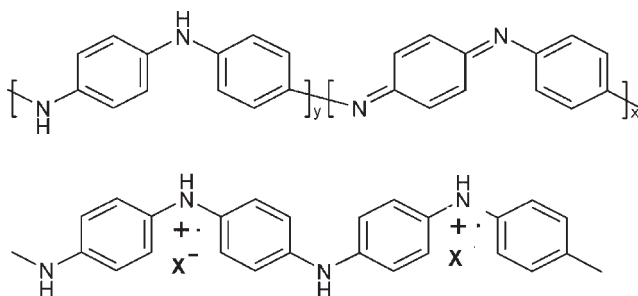
The unique and best combination of polyaniline properties such as low cost and easy to prepare monomer and polymer, high thermal and oxidative stability, possibility for polymer to be doped using a variety of *p* or *n*-dopants or using protonic inorganic or organic acids and its potential in commercial applications have attracted extensive attention in the last years.^[1–4] Polyaniline (PANI) can exist in three different oxidation (insulating) states (Scheme 1), in which *y* can vary from *y* = 0, fully oxidized form (pernigraniline base) to *y* = 1, fully reduced form (leucoemeraldine base). The intermediary oxidized state having *y* = *x* = 0.5 is known as emeraldine base. The most conducting form of PANI is known as emeraldine salt and usually is obtained directly by oxidative polymerization of aniline in aqueous acidic solutions or by protonation of the imine nitrogens of emeraldine base

with non-oxidizing inorganic or organic acids (HX).

The interactions of PANI with different polymeric acids as dopants improve the polyaniline processability and mechanical properties and miscible blends and composites can be obtained. The attractive forces between the two polymers are hydrogen bonds, ion-ion, dipole-dipole or acid-base interactions, depending on the polyacid chemical structure and complexation conditions. There are a lot of methods for synthesis of PANI composites and blends, mainly based on (electro)chemical polymerization of aniline in presence of polymer solutions, dispersions or emulsions, or blending of PANI with matrix polymers and they were recently reviewed.^[5] Macromolecular acids containing sulfonic groups such as poly(ethene sulfonic acid),^[6] poly(styrene sulfonic acid),^[6–13] poly(2-acrylamido-2-methyl-1-propane sulfonic acid)^[14] or carboxylic groups such as poly(acrylic acid)^[6,7,15] and polyamic acid^[16] have been synthesized and characterized. The aim of this paper is to present new results regarding chemical oxidative polymerization of aniline in presence of maleic acid copolymers and the thermal behavior of composites. Four maleic acid copolymers have been used as macromolecular acids and

¹ “Petru Poni” Institute of Macromolecular Chemistry,
41A Grigore Ghica Voda Alley, Iasi-700487
Fax: (+40) 0232 211299
E-mail: grim@icmpp.ro

² ICPE-CA Bucuresti, Splaiul Unirii 313, Bucuresti,
Romania

**Scheme 1.**

Chemical structure of undoped and doped polyaniline; X can be an inorganic or organic rest.

they have been synthesized by radical copolymerization of maleic anhydride with vinyl acetate, N-vinyl pyrrolidone, styrene and methyl methacrylate in 1:1 feed molar ratio, followed by hydrolysis. While the first three samples are alternating copolymers the last one has a 1:3 molar ratio between maleic anhydride and methyl methacrylate units. The proton of carboxylic groups reacts with imine nitrogen of polyaniline emeraldine base and changes it to emeraldine salt, the rest of macromolecular acid being the counterion. These multicomponent systems formed from a polymer with a high proton density and another one (polyaniline) as proton acceptor can be studied for application as proton-conductive materials for electrolyte membranes of fuel cells. For these applications, the polymer membranes

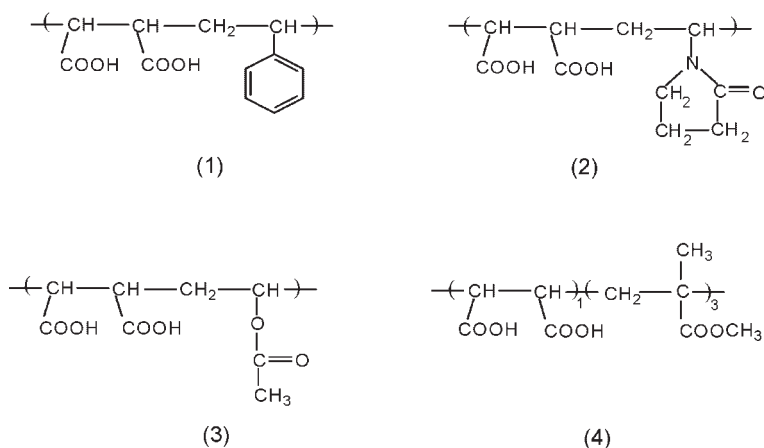
have to meet following requirements: proton conductivity higher than $0.01 \text{ S} \cdot \text{cm}^{-1}$, long-term stability under humidified and heated conditions and impermeability to hydrogen, methanol and oxygen.^[17]

Experimental Part

Materials

All solvents were purified by usual methods. Reagent grade aniline was vacuum distilled under nitrogen atmosphere just before use. Ammonium peroxydisulfate, N,N-dimethylformamide and other chemicals were commercially products (reagent grade) and used as received.

Maleic acid copolymers (Scheme 2) used as templates were prepared from copoly-

**Scheme 2.**

Chemical structure of maleic acid copolymers with styrene (1), N-vinyl pyrrolidone (2), vinyl acetate (3), and methyl methacrylate (4).

mers of maleic anhydride (MA) with vinyl acetate, N-vinyl pyrrolidone, styrene and methyl methacrylate, synthesized according to the published methods.^[18–21] The MA copolymers were hydrolyzed and neutralized with diluted NaOH aqueous solution, when copolymers of sodium maleate (NaM) were obtained. The solutions were desalted and the oligomers were removed by diafiltration until the filtrate conductivity was lower than 10 μ S and the NaM copolymers were recovered by freeze-drying. From these copolymers the free acid form was prepared by passing dilute solutions of sodium salts through an ion exchange column filled with Dowex 50WX 8 20–50 mesh sulfonic resins. The aqueous solutions of maleic acid copolymers were used after concentration in the diafiltration device.

Composite materials were synthesized by *in situ* chemical oxidative polymerization of aniline in presence of the four maleic acid copolymers. The reactions were carried out in aqueous solution of the copolymers using ammonium peroxodisulfate as oxidant. In a typical procedure, 0.1 ml of aniline was added to 10 ml 0.1M aqueous solution of maleic acid copolymer, in nitrogen atmosphere and the mixture was stirred at room temperature for 24 hours for acid-base interaction between carboxyl groups of maleic acid unit and aniline. Then the solution was cooled at 0 °C and oxidant (3:1 molar ratio *vs* aniline) was dropped and stirring was continued for 2 hours. Finally the reaction was carried out at room temperature for another 20 hours. The colored aqueous dispersions were dialysed using a cellulose membrane dipped in distilled water and air-dried to obtain a fine colored powder.

Characterization

FTIR spectra were recorded in KBr pellets on a DIGILAB-FTS 2000 spectrometer. DSC measurements were performed with a Mettler DSC-12E apparatus, in nitrogen and thermal analysis were carried out with a DERIVATOGRAPH Q-1500D (Budapest).

Composition of PANI/maleic acid copolymers was estimated from elemental analysis of nitrogen.

Results and Discussion

Four maleic copolymers having chemical structure presented in Scheme 2 have been synthesized by radical copolymerization of maleic anhydride with vinyl acetate,^[18] N-vinyl pyrrolidone,^[19] styrene^[20] and methyl methacrylate^[21] in 1:1 feed molar ratio and used as macromolecular acids instead of HCl in chemical oxidative polymerization of aniline. The first three samples are alternating copolymers while the last one has a 1:3 molar ratio between maleic anhydride/methyl methacrylate units. Maleic acid copolymers dissociate in two steps, the first –COOH group having a strong acid character, $pK_1 \sim 3.5$ –4 while the second one dissociates in the alkaline range, $pK_2 \sim 8.5$ –10, therefore it is undissociated in the experimental conditions.^[22,23] Therefore, interactions of acid-base and hydrogen-hydrogen type can appear between aniline and maleic acid copolymer with participation of the first and second carboxylic groups, respectively.

Chemical *in situ* oxidative polymerization of aniline using ammonium peroxodisulfate as oxidant and in presence of the maleic acid copolymers has carried out and very fine dispersions of polyaniline/copolymer with colors changing from brown, brown-dark, green and black during the polymerization were obtained. After dialysis and vacuum removing of the water, all samples are solid materials insoluble in water, with very fine dispersed particles and their color is more darkened than of their suspensions. They are soluble in strong polar solvents, such as DMF and DMSO and attempts to precipitate the composites by addition of water have failed. Even at 3:1 (vol) water/solvent, copolymer/polyaniline composites remain dissolved and they can be precipitated only by addition of a strong inorganic acid (HCl). The nitrogen percentage in PANI/maleic copolymers samples

Table 1.

Elemental analysis of polyaniline/maleic acid copolymer samples.

Sample	Maleic copolymer	N;exp. (%)	C; H; N; calcd. (%)	polyaniline/maleic acid unit ratio ^{a)}
Pernigraniline			80.00; 4.44; 15.55	–
Emeraldine base			79.56; 4.97; 15.47	–
Leucoemeraldine			79.12; 5.49; 15.38	–
PANI-1	1	9.01	71.82; 5.24; 6.98	1/0.60
PANI-2	2	9.93	64.71; 5.39; 10.29	1/1.17
PANI-3	3	8.24	62.66; 4.96; 7.31	1/0.78
PANI-4	4	9.25	62.31; 6.20; 4.69	1/0.20

^{a)} polyaniline structural unit was considered ($-\text{NH}-\text{B}-\text{N}=\text{Q}-$), where B and Q are benzenoid and quinoid rings, while for maleic acid copolymers the structural unit are presented in Scheme 2.

(Table 1) was used to approximate the composition of the materials.

The chemical oxidative polymerization of aniline in absence of acidic conditions has yielded to polyaniline with an emeraldine base structure containing both imine and amine units. The calculated nitrogen percentages for leucoemeraldine, emeraldine base and pernigraniline presented in the Table 1 are very close and practically couldn't be used to differentiate them. In presence of maleic acid copolymers, polymerization of aniline is expected to yield to emeraldine salt form where the first $-\text{COOH}$ group from maleic unit dope the imine nitrogens, the second one has a very low dissociation constant and protonation of another imine group is most probably due to $-\text{COOH}$ from other maleic unit. If only one carboxylic acid group from structural unit of the copolymer is able to dope PANI, the PANI would be fully doped in the 1:1 PANI/MA copolymer composites. From elemental analysis it results that the optimum complexation takes place between polyaniline and maleic anhydride/ N-vinyl pyrrolidone copolymer, a hydrophilic material that can dope and also form hydrogen bonds with polyaniline by undissociated COOH group and pyrrolidone rings. On the other hand, the unfavorable situation is observed for copolymer 4 that contains a hydrophobic comonomer (methyl methacrylate) in 3:1 molar ratio vs maleic acid units in polymer chain.

FTIR spectroscopy can bring valuable information regarding the formation of

PANI composites. The FTIR spectra of polyaniline emeraldine base (prepared in aqueous HCl and dedoped with ammonium hydroxide) and PANI 1–4 composites are presented in Figure 1 and 2. The broad band around $3420\text{--}3100\text{ cm}^{-1}$ is present in all spectra and is assigned to stretching vibration of NH_2 and NH asymmetric stretching vibrations and H-bonded NH groups^[2] while stretching vibrations of $\text{C}=\text{C}$ from benzenoid and quinoid rings are situated at 1491 and 1576 cm^{-1} , respectively and at 1300 cm^{-1} is $\text{C}-\text{N}$ stretching vibration. The peaks at 1132 , 806 , 708 and 611 cm^{-1} can be assigned to in-plane and out-of-plane vibrations of $\text{C}-\text{H}$ bonds from para-disubstituted aromatic rings. The presence of a long absorption tail above 2000 cm^{-1} , which masks the NH stretching vibrations and a broader band at about 1150 cm^{-1} in FTIR spectra of PANI-1, PANI-2, PANI-3 and PANI-4 suggests the protonation of imine groups of polyaniline by $-\text{COOH}$ from maleic copolymers.

FTIR spectra of maleic acid copolymers show characteristic absorptions for $-\text{OH}$ stretching vibrations ($2900\text{--}3600\text{ cm}^{-1}$), the $\text{C}=\text{O}$ stretching vibrations in the range $1720\text{--}1680\text{ cm}^{-1}$, 1400 and 1600 cm^{-1} (COO^- symm. and asymm.) and also 1290 ($\text{C}-\text{N}$ stretching in pyrrolidone ring), 1070 cm^{-1} ($\text{C}-\text{O}-\text{C}$ in vinyl acetate and methyl methacrylate copolymers), peaks that are also present in spectra of the corresponding PANI composites.

DSC and TGA measurements for PANI and PANI 1–4 were performed to obtain

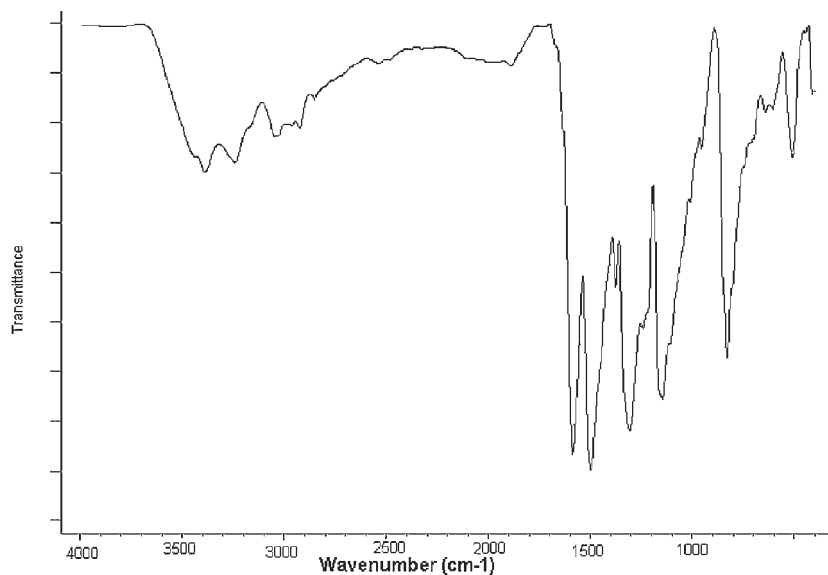


Figure 1.
FTIR spectrum (KBr pellet) of polyaniline emeraldine base.

information on thermal behavior in the temperature range of 20–750 °C and results are presented in Figure 3–5 and Table 2 and 3. DSC studies of PANI-emeraldine base and salt and their composites with maleic acid copolymers (Figure 3) does not

exhibit any specific thermal transition in the range 40–180 °C that should be assigned to glass transitions. Due to the intrinsic structure of the polyaniline chain, its glass transition temperature is higher than the thermal decomposition. However, polyaniline/maleic

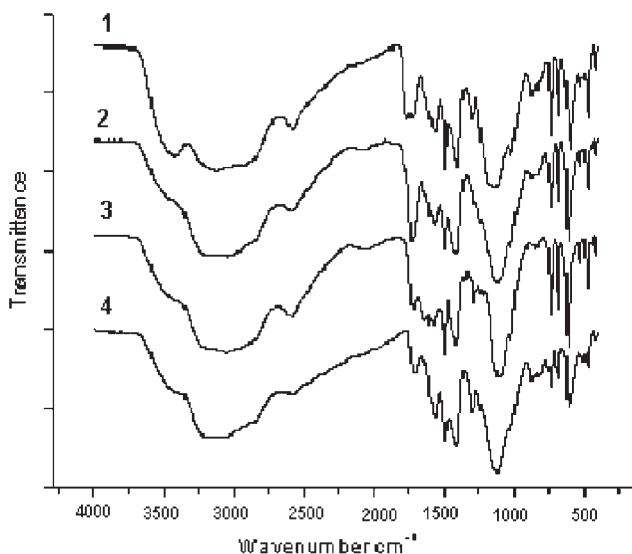


Figure 2.
FTIR spectra (KBr pellet) of PANI 1 – PANI 4 composites (curves 1 to 4, respectively).

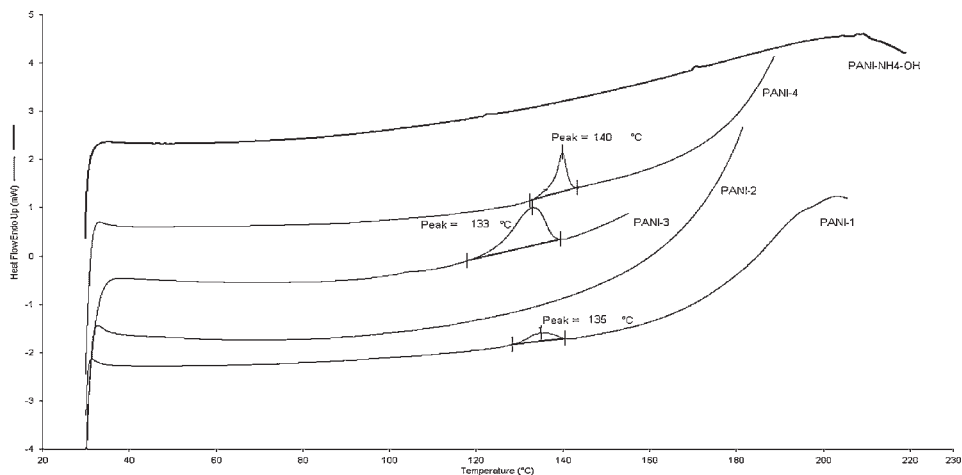


Figure 3.

DSC scans (nitrogen atmosphere, heating rate = 10 °C/min) for PANI 1–4 and PANI emeraldine base (obtained from PANI-HCl by dedoping with ammonium hydroxide).

acid copolymers composites (with exception of PANI-2) show endothermic peaks between 133–140 °C that cannot be assigned to a melting process because all copolymers are amorphous materials but can be associated with anhydriization of COOH groups (intra- and intermolecular reaction) and removing of adsorbed water.

Thermogravimetric analysis of HCl doped polyaniline (in nitrogen) shows three steps weight loss, at ~100, 200 and 500 °C while undoped polyaniline (base form)

shows only two major decomposition step at ~100 and 500 °C. The last step is assigned to the thermal degradation of polyaniline chain while the first two steps are attributed mainly to the removing of moisture and volatile impurities and dopant, respectively.^[24,25] Thermal analysis of maleic acid copolymers evidences four or five weight loss processes around 75–100 °C, 150–175 °C, 275 °C, 350 °C and 525–575 °C. The first two processes are assigned to the loss of the volatiles and moisture from samples and

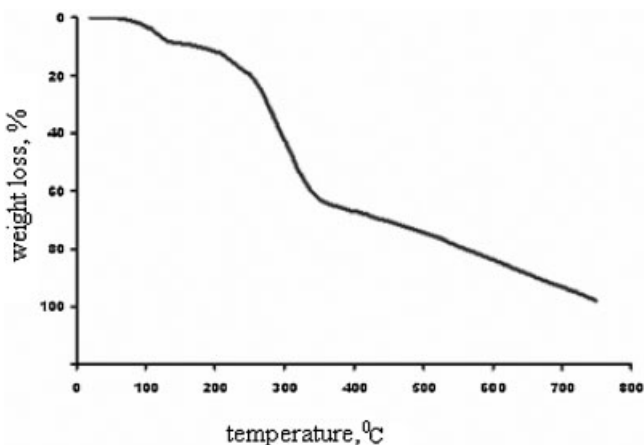


Figure 4.

TGA thermogram of PANI-3.

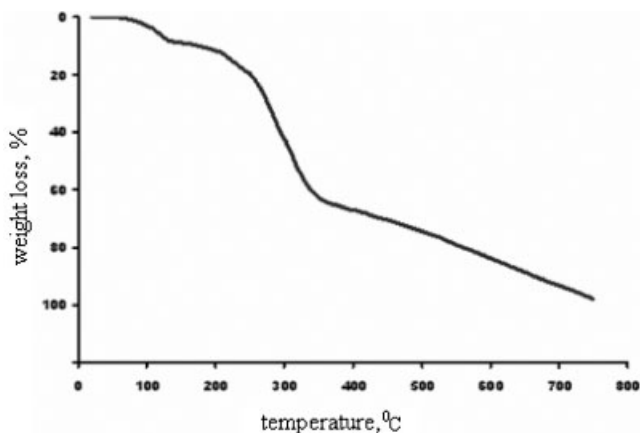


Figure 5.

TGA thermogram of PANI-4.

Table 2.

Thermogravimetric characteristics of maleic acid-vinyl acetate copolymer (3) and PANI-3.

Step	Copolymer 3			PANI-3		
	Temperature range °C	T_{\max} , °C	Weight loss, %	Temperature range °C	T_{\max} , °C	Weight loss, %
I	30–125	107	2	30–155	125	8,0
II	125–200	170	6,4	155–240	212	10,0
III	200–317	273	36,8	240–350	315	44,0
IV	317–460	350	22	350–490	370	11,2
V	460–665	577	29,6	490–700	570	24,5

T_{\max} is temperature of the maximum decomposition.

Table 3.

Thermogravimetric characteristics of maleic acid-methyl methacrylate copolymer (4) and PANI-4.

Step	Copolymer 4			PANI-4		
	Temperature range °C	T_{\max} , °C	Weight loss, %	Temperature range °C	T_{\max} , °C	Weight loss, %
I	25–105	76	0,6	30–160	110	9,2
II	105–234	145	5,2	160–235	205	9,6
IV	234–445	344	80	235–370	330	45,3
V	445–565	528	11,2	370–690	580	33,9

T_m is temperature of the maximum decomposition.

elimination of water molecules in intra and/or intermolecular anhydization of COOH groups. The third step is present only in vinyl acetate copolymers (3) and is associated to acetic acid elimination process. The last two steps are attributed to the thermal destruction of polymers by depo-

lymerization, decarboxylation and degradation processes. Thermogravimetric analysis of PANI-maleic acid copolymers evidences also four or five weight loss processes and their assignment is similar with that for individual components. However, a shifting of temperature range for all

steps at higher values is observed, polyaniline having a beneficial effect on thermal behavior of composites.

Conclusions

New polyaniline composites have been synthesized by *in situ* chemical oxidative polymerization of aniline in aqueous solutions of four maleic acid copolymers and characterized by spectroscopic methods and thermal analysis. Composite materials have an improved thermal stability and solution processability compared to every component.

Acknowledgements: Authors thank the Romanian National Authority for Scientific Research for financial support (CEEX project 88/2005, RELANSIN program).

- [1] F. Lux, *Polymer* **1994**, 35, 2915.
- [2] E. T. Kang, K. G. Neoh, K. L. Tan, *Prog. Polym. Sci.* **1998**, 23, 277.
- [3] J. Anand, S. A. Palaniappan, D. N. Sathyanarayana, *Prog. Polym. Sci.* **1998**, 23, 993.
- [4] N. Gospodinova, L. Terlemezyan, *Prog. Polym. Sci.* **1998**, 23, 1443.
- [5] A. Pud, N. Ogurtsov, A. Korzhenko, G. Shapoval, *Prog. Polym. Sci.* **2003**, 28, 1701.
- [6] J. H. Hwang, S. C. Yang, *Synth. Met.* **1989**, 29, E271.
- [7] J. M. Liu, S. C. Yang, *J. Chem. Soc. Chem. Commun.* **1991**, 1529.
- [8] S. Li, H. Dong, Y. Cao, *Synth. Met.* **1989**, 29, E329.
- [9] B. D. Malhotra, S. Ghosh, R. Chandra, *J. Appl. Polym. Sci.* **1990**, 40, 1049.
- [10] Y. Kang, M. H. Lee, S. B. Rhee, *Synth. Met.* **1992**, 52, 319.
- [11] Y. H. Liao, K. Levon, *Polym. Adv. Technol.* **1995**, 6, 47.
- [12] L. A. Samuelson, A. Anagnostopoulos, K. S. Alva, J. Kumar, S. K. Tripathy, *Macromolecules* **1998**, 31, 4376.
- [13] W. Liu, A. L. Cholli, R. Nagarajan, J. Kumar, S. Tripathy, F. F. Bruno, L. A. Samuelson, *J. Am. Chem. Soc.* **1999**, 121, 71.
- [14] M. Lapkowski, *Synth. Met.* **1993**, 55, 1558.
- [15] A. A. Chen, H. T. Lee, *Macromolecules* **1995**, 28, 2858.
- [16] M. Angelopoulos, N. Patel, R. Saraf, *Synth. Met.* **1993**, 55, 1552.
- [17] K. D. Kreuer, *J. Membr. Sci.* **2001**, 185, 29.
- [18] G. C. Chitanu, I. Popescu, A. Carpov, *Rev. Roum. Chim.* **2006**, 51, 915.
- [19] E. Csákvári, M. Azori, F. Tüdös, *Polym. Bull.* **1981**, 5, 413.
- [20] G. T. Verlag, *Makromolekulare Stoffe, E 20: Methoden der organischen Chemie*, Houben-Weyl, Stuttgart **1987**, 1239.
- [21] G. C. Chitanu, I. Popescu, A. Carpov, *Rev. Roum. Chim.* **2007**, 52, 135.
- [22] G. C. Chitanu, M. Rinaudo, J. Desbrieres, M. Milas, A. Carpov, *Langmuir* **1999**, 15, 4150.
- [23] G. C. Chitanu, M. Rinaudo, M. Milas, A. G. Anghelescu-Dogaru, A. Carpov, *Synth. Polym. J.* **2000**, 7, 119.
- [24] Y. Wei, K. F. Hsueh, *J. Polym. Sci.: Polym. Chem.* **1989**, 27, 4351.
- [25] H. S. O. Chan, P. K. Oh, E. Khor, M. M. Tan, *Synth. Met.* **1989**, 31, 95.