Polymer Bulletin 48, 407-414 (2002)

Polymer Bulletin

Modification of porous copolymers network based on acrylonitrile

Erika Carneiro Riqueza[1], Alcino Palermo de Aguiar[1](✉), Luiz Claudio de Santa Maria (✉),[2] Mônica Regina Marques Palermo de Aguiar[2]

[1]Departamento de Engenharia Química, Instituto Militar de Engenharia, Praça General Tibúrcio, 80 Rio de Janeiro/RJ, CEP 22290-270, Brasil
e-mail: alcino@epq.ime.eb.kr, Fax: +55 21 2546-7059
[2]Grupo de Polímeros (GPol), Instituto de Química, Universidade do Estado do Rio de Janeiro, R. São Francisco Xavier 524, Pavilhão Haroldo Lisboa da Cunha, Rio de Janeiro/RJ, CEP 20559-900, Brasil
e-mail: lcsm@uerj.br, Fax: +55 21 2587 7322

Received: 6 October 2001/Revised version: 2 April 2002/ Accepted: 11 April 2002

Summary

The preparation of a chelating ion-exchange network based on acrylonitrile was carried out by chemical modification with hydroxylamine. The beads of resin were synthesized by aqueous suspension copolymerization of acrylonitrile (AN), styrene (STY) and divinylbenzene (DVB). The influence of diluent used in the suspension polymerization on the structure of the resulting copolymers was evaluated. The diluents employed were heptane (HEP), toluene (TOL) and anisole (ANI). It was found that the AN incorporation into copolymer structure was dependent on the diluent used. Conversion of nitrile groups into the amidoxime was conducted by treatment with hydroxylamine under alkaline solution. The resins were characterized by apparent density, surface area, average pore diameter, elemental analysis (CHN), FTIR and optical microscopy. Based on the results obtained, it was possible to control the porosity by diluent employed in the synthesis and to modify chemically a resin containing nitrile groups by hydroxylamine reaction.

Introduction

Functionalized cross-linked polymers have gained great importance in many fields of scientific research as well as for industrial applications, which continues increasing due to several possibilities of modification of their chemical and physical properties. Organic and inorganic sorbents functionalized with complexing groups have been developed and reported in the literature[1-7]. As it has been reported, the porous structure is very important to this material. This porous structure is responsible for its performance and can be controlled by the concentration of the crosslinking agent and by the concentration and nature of the porogen system employed during the copolymerization reaction [8,9].

Polymers that present nitrile groups display some uncommon features. In polymers based on acrylonitrile, dipole-dipole interactions among nitrile groups make it crystalline. The degree of crystallinity can be high and even in crosslinked acrylonitrile/divinylbenzene (AN/DVB) copolymers a significant amount of crystallites can be detected[10-16]. It has been found that polymers network based on acrylonitrile were macroporous regardless of the crosslinker level, thus indicating importance of additional ‘physical’ crosslinks.

Resin based on acrylonitrile is easy to prepare and presents a reactive pendant group (nitrile group), which can be modified by different kinds of reagent through nucleophilic addition[17]. However, normally, the degree of modification is low due to poor accessibity of nitrile groups[18-23]. Hence, the aim of this work is to present simple way to enhance AN incorporation into resin structure and to introduce the amidoxime group by reaction with hydroxylamine.

Experimental part

Materials – Acrylonitrile (AN) and divinylbenzene (DVB, grade of 45%, containing a mixture of DVB and ethylvinylbenzene) were kindly offered by Nitriflex (Brazilian Co.) and styrene (STY) was donated by Petroflex (Brazilian Co.) and used as received; α,α’-azo-bis-isobutyronitrile (AIBN) was donated by Metacril do Brasil and was recrystallized in methanol; hydroxylamine hydrochloride, gelatin, 2-butanone, propanone, NaCl, NaOH, n-heptane, toluene, methanol were purchased from Vetec (Brazilian Co.) and anisole (Merck) with P.A. degree and used as received.

Preparation of resin based on acrylonitrile – AN/DVB and AN/STY/DVB copolymers were obtained in a typical glass reactor (1000 mL) fitted with mechanical stirrer using the suspension polymerization technique. Aqueous phase (AP) was composed by gelatin and 2-hydroxyethyl-celullose (0.3 and 0.2 wt.-% with respect to AP, respectively) and Na_3PO_4 (2 wt.-% in relation to AP). The organic phase (OP) was composed by monomers mixture (0.28 mol of AN, 0.14 mol of STY and 0.28 mol of DVB or 0.42 mol of AN and 0.28 mol of DVB), diluent, namely heptane, toluene and anisole, mixed or not (150 % v/v with respect to the monomers) and AIBN used as initiator (1.0 mole % with respect to the monomers). OP was added slowly to AP previously prepared under stirring at room temperature, employing AP/OP ratio = 3/1. These two phases were maintained under stirring (400 rpm) at room temperature during 10 min. Hence, the suspension copolymerization system was kept under stirring at 70ºC during 24 hours. The resin beads was thoroughly washed with hot water (8 portions of 500 mL) and with propanone and dried at 60ºC. The yield of copolymers beads was 41-75% and they have presented a narrow particle size distribution (210-250 μm).

Chemical modification of resin – Preparation of alkaline hydroxylamine solution: about 4.5 g of hydroxylamine hydrochoride was dissolved in 32 mL methanol-water (5:1) mixture. The HCl of NH_2OH was neutralized by NaOH solution and the precipitate of NaCl was removed by filtration. The pH of the reaction solution was maintained at pH 10-11 by adding NaOH solution. The modification of resins was carried out by reacting the AN/DVB (ER06 - resin that presents a large AN content) with the alkaline hydroxylamine solution at

85ºC for 24 or 48 h.

Resin characterization – The bead size distribution was determined by different sieves. The specific surface area (in m^2/g), average pore diameter (Å) and pore volume in the dry state (cm^3/g) were determined by the BET method from low-temperature nitrogen adsorption isotherms (ASAP Micromeritics 2000) at 77 K using a high-vacuum volumetric apparatus. The samples were degassed at 100ºC/1mPa for 3 h. Surface area, average pore diameter and pore volume of ER02 and ER05 resins were determined by mercury porosimetry (Quanta Chrome-Auto Scan mercury porosimeter model SP33D). Carbon, hydrogen and nitrogen contents were determined by elemental analysis (CHN Perkin-Elmer 2400). The chemical modification of nitrile groups was verified by infrared techniques (FTIR – Perkin-Elmer Spectrum One) in KBr pellets. The morphological characteristics were observed with a stereo optical microscope (Olympus SZ10). Resins were also characterized at scanning electron microscope (Jeol JSM – 5800LV). The beads were coated with carbon film and their external and internal parts were observed using 10 kV acceleration electron beam. The swelling degree (%S) of copolymers in different solvents (namely, toluene, n-heptane, water, methanol and anisole) before amidoximation was calculated from the following relation $\%S = [(v_1 - v_0)/v_0].100$, where v_1 is the volume of swollen resin after 24 hours and v_0 is the volume of dry state[24].

Results and discussion

The copolymers beads of acrylonitrile (AN), styrene (STY) and divinylbenzene (DVB) with a nominal crosslinking degree 40 % molar of DVB (ER01, ER02 and ER03) were obtained by suspension polymerization of monomers. The portion of STY (20% molar) in subsequent samples (ER04, ER05 and ER06) was replaced by AN and polymerization conditions were exactly the same as in the case on AN/STY/DVB copolymers. In order to obtain copolymers containing high nitrile group content, resins based on AN were prepared using different types of diluents at a constant DVB amount. Table 1 summarizes the synthesis parameters and chemical composition of resins obtained. Figure 1 shows the FTIR spectra of copolymers synthesized. It was observed that the bands of nitrile groups (CN stretching at $2237cm^{-1}$) were presented for all spectra, indicating AN incorporation. As it can be seen on Table 1, the type of diluent had an important role on the AN incorporation. The resin obtained with anisole (ANI) (ER06) used as diluent has presented higher AN incorporation than those obtained with n-heptane (HEP) or toluene (TOL) alone or mixed. Priorly, it was observed a lightly increase in the nitrogen content of the resin obtained with the major amount of TOL which possesses a solubility parameter similar to that calculated for poly(DVB/STY), but is a poor solvent for poly(AN). As it was pointed out by Okay[23,25], during STY-DVB copolymerization, TOL remains mainly in the polymer gel, resulting in the formation of an expanded network. One can assume that in the case of AN-DVB, with large portion of DVB in the monomer mixture, a similar situation occurs. TOL is able to swell the gel of poly(STY-DVB) or poly(DVB) formed in early polymerization stages due to the highest reactivity of DVB compared to AN. Thus, the AN polymerization takes place in the swollen gel of poly(STY-DVB) or poly(DVB) or on surface of agglomerates. When the AN amount in the monomer mixture increases, the inhomogeneity of polymer network also increases due to the poor solvation conditions. Moreover, TOL is molecule of low polarity (dielectric constant $\varepsilon = 2.38$ and dipole moment $\mu = 0.36$ D)[26] and consequently it is able to separate AN associates[25]. For this reason, TOL was replaced by ANI (dielectric constant $\varepsilon = 4.30$ and dipole moment $\mu = 1.38$ D). Although there is no information about the solubility parameter of this solvent in relation to poly(STY/DVB) and poly(AN)[27], it seems that this diluent is a better solvent for the polymer formed than TOL or HEP ($\varepsilon = 1.92$ and $\mu \approx 0$).

Table 1. Synthesis data and copolymers chemical composition

Sample	Monomer in the feed[a)] (mol-%)	Diluents[b)]	Nitrogen content[c)] (%)	AN content[d)] (%)	Yield (%)
ER01	40 AN/20 STY/40 DVB	70 HEP/30 TOL	1.9	32	71
ER02	40 AN/20 STY/40 DVB	100 HEP	1.9	32	56
ER03	40 AN/20 STY/40 DVB	100 TOL	2.9	49	64
ER04	60 AN/40 DVB	100 TOL	4.5	45	54
ER05	60 AN/40 DVB	70 HEP/30 TOL	2.4	24	41[e)]
ER06	60 AN/40 DVB	100 ANI	6.9	69	75

a)Polymerization conditions: aqueous phase (AP) composed by gelatin and 2-hydroxyethyl-celullose (0.3 and 0.2 wt.-% with respect to AP, respectively) and Na_3PO_4 (2 wt.-% in relation to AP); the initiator used was AIBN (1.0 mol- % with respect to the monomers) – HEP = n-heptane; TOL = toluene; ANI = anisole; b) 150 vol.-% of dilution (volume ratio between monomers and diluents 1:1); c) Elemental analysis (CHN); d) Acrylonitrile incorporation in relation to the amount used in the feed; e) not optimized yield

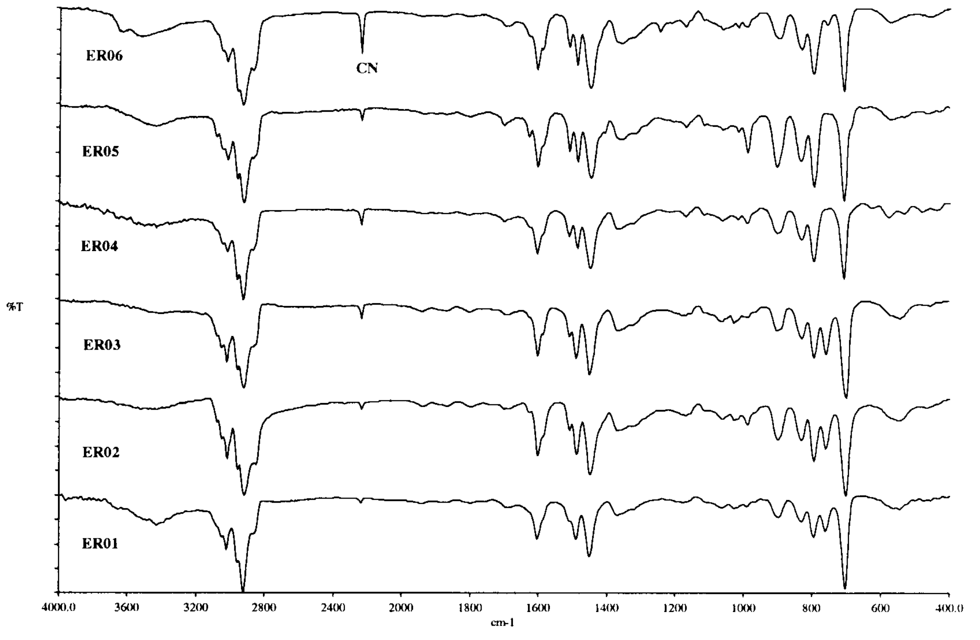


Figure 1. Spectra of FTIR of AN copolymers.

The higher AN incorporation in the ER06 resin than the other ones can be attributed to its partial solubility in water (7.35 parts in ration to 100 parts of water) [26]. Hence, it is possible to assume that the distribution coefficient of AN in ANI between aqueous and organic phases is higher than HEP. It can be attributed to the better affinity of AN to polar solvents compared to nonpolar one. Comparing TOL and ANI, the best solvent was ANI maybe because of its highest polarity.

As it can be seen from Tables 2 and 3, the copolymers obtained differ in their porosity (bulk density, pore diameter, specific surface area and appearance) and swelling properties in different solvents. In a general way, it can be noted that copolymers obtained with TOL or ANI presented higher bulk density (ER03, ER04 and ER06) than those obtained with HEP or a TOL/HEP mixture. It could be observed that the ER02 resin obtained with HEP presented lower density and bigger pore volume compared to other ones. These results can be explained by the higher degree of phase separation, which occurred in great extension during the copolymerization process. On the other hand, the copolymer obtained in the presence of polar diluent (ANI) can be characterized with higher density (0.5 g/cm^3), with more closely packed structures than those synthesized in HEP or TOL/HEP mixture. The resins obtained with the mixture TOL/HEP (ER01 and ER05) presented intermediate porosity (Table 2). The porous structure was confirmed by swelling in different solvents (Table 3). All dense resins (ER03, ER04, ER06) have swollen very well in methanol, toluene, anisole and even heptane (a poor solvent for acrylonitrile polymers). It indicates that these resins are mesoporous. As it can be noted on Table 2, this feature was confirmed by medium pore diameter of these copolymers that are smaller than those copolymers obtained with HEP or HEP/TOL mixture. In addition, the specific surface areas of dense copolymers are large due to the mesoporosity. It is possible to conclude that there is a correlation of the pore diameter, bulk density and swelling on the diluent composition used in the copolymer synthesis. As the polarity of solvent increases, the solvating power of the diluent increases leading to a less pronounced phase separation, decreasing the copolymers porosity. As expected, the increase of pore size has provoked a reduction in the density and in the swelling, since there are larger pores.

Table 2. Porous characteristics of AN copolymers

Sample	Diluents	Bulk density (g/cm^3)	Medium Pore Diameter (Å)	Pore Volume (cm^3/g)	Specific area (m^2/g)	Appearence$^{d)}$
ER01	HEP/TOL$^{a)}$	0.21	113$^{b)}$	0.16	57	O
ER02	HEP	0.18	850$^{c)}$	2.50	121	D
ER03	TOL	0.42	75$^{b)}$	0.63	339	T/O$^{e)}$
ER04	TOL	0.37	78$^{b)}$	0.83	425	T/O
ER05	HEP/TOL$^{a)}$	0.16	565$^{c)}$	0.026	273	O
ER06	ANI	0.50	70$^{b)}$	0.32	184	T/O$^{f)}$

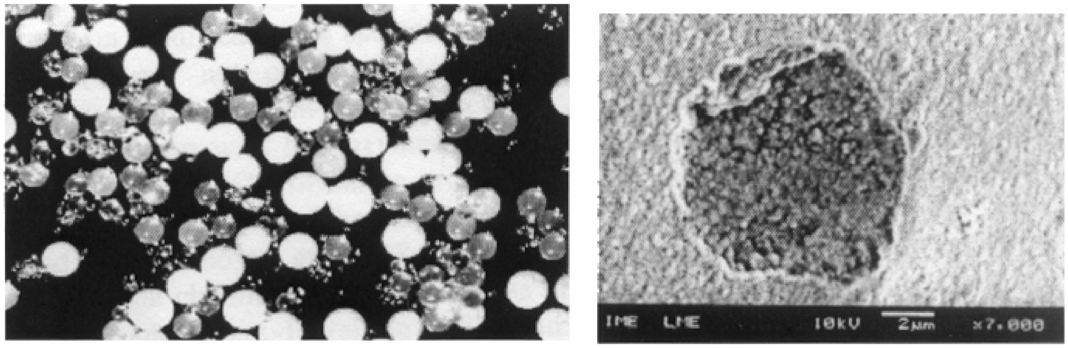
a) 70HEP/30TOL; b) measurement by BET; c) measurement by mercury porosimetry; d) T = transparent; D = diaphanous; O = Opaque; e) predominant O; f) T/D some beads are T and some others are D.

Table 3. Swelling percentage (%S) of copolymers in different solvents

Sample	Diluents	%S in Methanol	%S in Toluene	%S in Water	%S in Heptane	%S in Anisole
ER01	HEP/TOL[a)]	10	44	0	17	0
ER02	HEP	0	34	0	0	33
ER03	TOL	73	90	3	73	87
ER04	TOL	46	93	3	77	83
ER05	HEP/TOL[a)]	20	23	2	30	25
ER06	ANI	120	113	7	100	156

a) 70HEP/30TOL

Figure 2a shows the optical micrography of copolymer beads obtained with ANI as diluent (ER06). It is possible to note that there are diaphanous beads and opaque ones, showing a porous structure between microporous and mesoporous. Figure 2b shows the scanning electronic micrography of this resin, confirming the heterogeneity of porous structures in this resin.

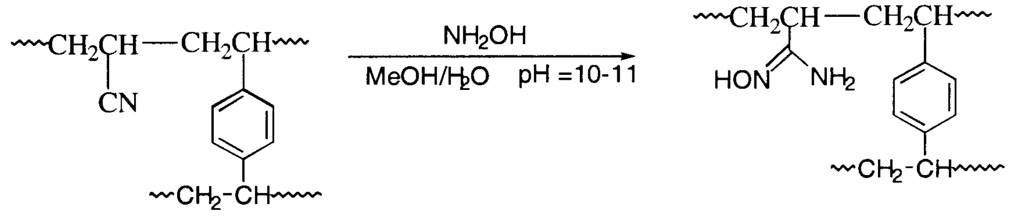


a) b)

Figure 2. a) Optical microscopy photomicrography of AN/DVB beads synthesized with ANI as diluent; **b)** Scanning electronic micrography (SEM) of the internal and external surfaces of AN/DVB beads synthesized with ANI as diluent (magnification x 7000)

As shown on Table 2, the appearance of copolymer beads was significantly affected as their porosity increased. This is related to the differences in the porosity degree. In the microporous-type copolymers, the structures are homogeneous and consequently the beads are diaphanous. On the contrary, porous copolymers consist of heterogeneous crosslinked structure formed by the agglomeration of microspheres inside the beads and exhibit an opaque appearance due to the light scattering in their irregular structures. It is possible that the copolymers containing AN units have, similar to poly(AN), semicrystalline structures in which ordered regions can act as additional 'physical' crosslinks. These crosslinks result in a rise in stiffness of the macromolecules and make the formation of porous structure easier. Replacing a nonpolar solvent (TOL or HEP) by a polar one (ANI) should affect the molecular packing. The AN/DVB and STY/AN/DVB copolymers obtained in the presence of good solvent presented higher density (with more closely packed structures) than those synthesized in a poor solvent. Thus, the copolymer obtained from good solvent should have more flexible networks.

The incorporated amount of AN in the copolymer should enhance the exposition of CN groups which enable these copolymers to be more easily anchor the metal ions. The amidoximation reaction was evaluated (reaction times are 24 or 48 hours) using the ER06, as represent in Scheme 1.



Scheme 1. Amidoximation reaction on the resin based on acrylonitrile/divinylbenzene

Figure 4 shows the typical spectra of unmodified and modified resins at the same analysis conditions. The presence of a band at 2238 cm^{-1} related to CN group on modified resins spectrum has shown that the modifications of nitrile groups were not complete. However it is important to note that the hydroxylamine reaction was conducted in a solid phase. The IR spectrum of modified resin with hydroxylamine exhibited a broad band observed in the 3650-3340 cm^{-1} (OH of oxime group)[27]. The C=N of the oxime group was observed at 1655 cm^{-1}. The band observed at 910 cm^{-1} is assignable to the N-O bond of the oxime group[28-31]. Although the ER06 resin presents low porosity the chemical modification was efficient. It was due to exposition of nitrile groups by good swelling of ER06 in the solvent employed.

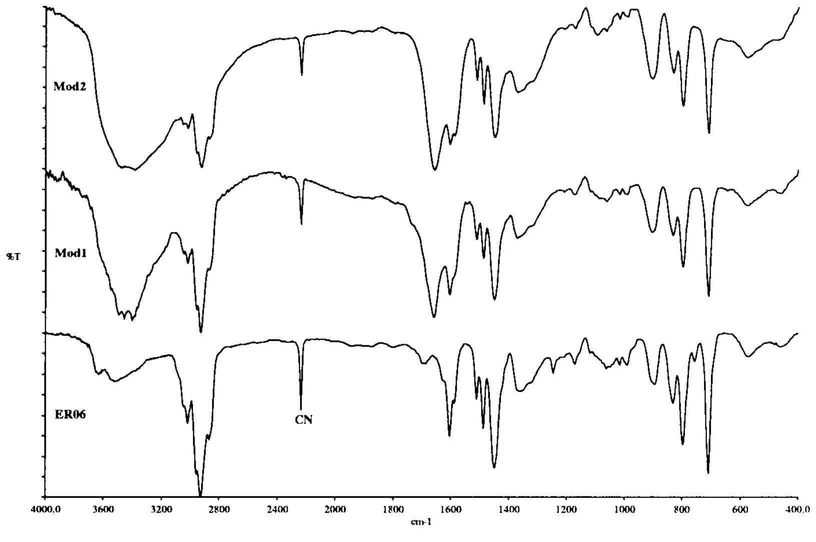


Figure 4: Spectra of FTIR of unmodified (ER06) and modified resins (Mod1 Mod2) with hydroxylamine as a function of the reaction time: Mod1 during 24 hr and Mod2 during 48 h

Acknowledgements. E.C.R. acknowledges the CAPES financial support. The authors also thank the CNPq, FAPERJ and PRONEX (IMA/UFRJ, COPPE/UFRJ, IQ/UERJ) for the financial support. We are grateful to Metacril do Brasil, Petroflex and Nitriflex for monomers and initiator donation. Thanks also go to Nitriflex for the CHN analyses.

References

[1] M.R. Lutfor, S. Silong, W. Md Zin, M.Z. Ab Rahman, M. Ahmad, J. Haron, Eur. Polym. J. 36 (2000) 2105.
[2] B.N. Kolarz, A.W. Trochimczuk, M. Wojaczynska, M. Drewniak, Angew. Makromol. Chem. 217 (1994) 19.
[3] F. M.B. Coutinho, S.M. Rezende, Celina C.R. Barbosa, React. Func. Polym. 49 (2001) 235.
[4] A. Boudakgi, J. Jezierska, B.N. Kolarz, Makmol. Chem., Macromol. Symp. 59 (1992) 343.
[5] B.N. Kolarz, A. Trochimczuk, M. Wojaczynska, Angew. Makromol. Chem. 193 (1991) 21.
[6] M. Wojaczynska, B.N. Kolarz, Makromol. Chem. 193 (1992) 2259.
[7] A. W. Trochimczuk, B.N. Kolarz, Eur. Polym. J. 36 (2000) 2359.
[8] C.T. Lima Luz, F.M.B. Coutinho Eur. Polym. J. 36 (2001) 547.
[9] C.T. Lima Luz, F.M.B. Coutinho Polymer 42 (2001) 4931.
[10] F. Vermon, W. Md. Zin, Anal. Chim. Acta 123 (1981) 309.
[11] B.N. Kolarz, D. Jermakowicz-Bartkowiak, A. Trochimczuk, Eur. Polym. J. 34 (1998) 1191.
[12] H. Egawa, T. Nonaka, K. Tsukamoto, Polym. J. 23 (1991) 1037.
[13] D. Baralkiewicz, H. Gramowska, J. Zerbe, J. Siepak, Chem. Anal. 37 (1992) 641.
[14] N. Pekel, N. Sahiner, O. Güven, Rad. Phys. Chem. 59 (2000) 485.
[15] M.B. Colella, S. Siggia, M. Barnes, Anal. Chem. 52 (1980) 967.
[16] R.A. Beauvais, S.D. Alexandratos, React. Func. Polym. 36 (1998) 113.
[17] L.C. Santa Maria, M.C.V. Amorim, M.R.M.P. Aguiar, P.I.C. Guimarães, M.A.S.Costa, A.P.Aguiar, P.R. Rezende, M.S. Carvalho, F.G. Barbosa, J.M. Andrade, R.C.C. Ribeiro, Reac. Func. Polym. 49 (2001) 133.
[18] I.M. Abrams, J.R. Millar, React. Func. Polym. 35 (1997) 7.
[19] A. Trochimczuk, J. Hradil, B.N. Kolarz, F. Svec, React. Func. Polym. 9 (1988) 135.
[20] A. Trochimczuk, J. Hradil, B.N. Kolarz, F. Svec, Polym. Bull. 20 (1988) 149.
[21] A. Boudakgi, J. Jezierskaz, B.N. Kolarz, Makromol. Chem., Macromol. Symp. 59 (1992) 343.
[22] V. Bulmus, K. Kesenci, E. Piskin, React. Func. Polym. 38 (1998) 1.
[23] O. Okay, Prog. Polym. Sci. 25 (2000) 711.
[24] O.Okay, E. Soner, A. Grungor, T. I. Balkas, J. Appl. Polym. Sci. 31 (1986) 1785.
[25] O. Okay, Angew. Makromol Chem. 157 (1988) 1.
[26] D.R.Lide, Handbook of Chemistry and Physics, 78th Edition, CRC, New York, 1997
[27] J. Brandrup, E.H. Immergut, Polymer Handbook, 3rd Edition, Wiley, New York, 1989.
[28] A. Chapiro, Z. Mankowski, Eur. Polym. J. 17 (1981) 472.
[29] D.G. Neilson, R. Roger, J.W.M. Heatlie and L.R. Newlands, Chem. Rev. 70 (1970) 151.
[30] A. Bigotto, Can. J. Chem. 32 (1954) 858.
[31] K. Nakanishi and P.H. Solomon – "*Infrared absorption spectroscopy*", Lolden-Day, San Francisco, 1977.