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The synthesis of poly(MA-*alt*-NIPA) copolymer, spectroscopic characterization, and the investigation of solubility profile-viscosity behavior

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Abstract

Alternating copolymer of maleic anhydride (MA) with *N*-isopropylacrylamide (NIPA) has been synthesized. Spectral characterization of this copolymer has been achieved by FTIR, Raman, ^{1}H, ^{13}C NMR spectroscopic methods. Besides hydrodynamic behavior of the copolymer has been also investigated by viscometric method for comparison with that obtained from the solubility profile through algorithmic calculations. As a consequence of the algorithmic calculations DMSO has been determined as the best solvent for the copolymer, poly(MA-*alt*-NIPA), which is also supported by the viscometric results.

Keywords: Poly(MA-*alt*-NIPA); Alternating copolymers; Solubility; Solubility parameter; Viscometry; FTIR; NMR; Raman

1. Introduction

Homo- and copolymers of *N*-isopropylacrylamide (NIPA) exhibited pH and thermal sensitivity and were used in biologically active systems (in protein conjugation) as cation-active polymers soluble in water and physiological medium (Chee, Rimmer, Soutar, & Swanson, 1997; Chen & Hoffman, 1995; Chen & Hsu, 1997; Ringsdorf, Venzmer, & Vinnik, 1991), as well as carrier system for DNA delivery (Hinrichs, Schuurmans-Nieuwenbroek, Vatering, & Hennink, 1999), for affinity separation of genotoxins (Umeno & Maeda, 1997) and as reversible bioconjugates (Kim & Park, 1999). Recently, synthesis and characterization of cationic stimuli-responsive acrylic acid-terminated poly(*N*-isopropylacrylamide) [poly(NIPA)], potentially useful as carrier for gene delivery, conjugates of poly (NIPA) with amino acids as prodings, antitumor active binary, and ternary copolymers of maleic anhydride, vinyl acetate, and acrylic acid (or 2,3-dihydropyran) have been reported (Bulmuş, Patır, Tuncel, & Pişkin, 2001; Dinçer, İbrişoğlu, & Pişkin, 2001).

Alternating copolymers of maleic anhydride can be regarded as preactivated polymers due to the presence of anhydride moieties susceptible to the reaction with a primary amine of a biomolecule (Veron, Bignicourt, Delair, Pichot, & Mandrand, 1996). Acrylamide and its derivatives can undergo alternating copolymerization with maleic anhydride under the given conditions (Kabanov, Zubov, & Semchikov, 1987; Rzaev, 1984, 2000). These copolymers are potentially useful as flocculants, for purification of industrial waste water, as coatings for microcapsule production and for paper dry-strength agents (Trivedi & Culberston, 1982).

Solubility parameter is one of the key parameters for selecting solvents in industry, characterizing surfaces, predicting solubility and degree of rubber swelling, polymer compatibility, chemical resistance, and permeation rates, and for numerous other applications. There is also much

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interest in utilizing solubility parameter for rationally designing new processes, such as the supercritical fluid, the coating, and the drug delivery processes (Barton, 1985; Bustamante & Pena, 1998; Hansen, 1967, 1999, 2004; Kaplan-Can, Barsbay, Güner, & Rzaev, 2006).

The central principle behind the use of δ is the historic alchemist maxim, “similia similibus solvuntur” (“like dissolves like”), probably, the oldest rule of solubility. This rule can, indeed, be a good guide in the study of solubility, as long as we can also define with sufficient precision the degree of likeness in the given system.

The enthalpy of mixing, given by,

$$\Delta H_m/V = \phi_1\phi_2(\delta_1 - \delta_2)^2 \qquad (1)$$

where δ_1 and δ_2 are the solubility parameters, ϕ_1 and ϕ_2 are the volume fractions of both substances and V is the total volume of the mixture, predicts that $\Delta H_m = 0$ if $\delta_1 = \delta_2$, so that two substances with equal solubility parameters should be mutually soluble due to the negative entropy factor. As the difference between δ_1 and δ_2 increases, the tendency towards dissolution decreases (van Krevelen, 1997). However, these predictions with the Hildebrand solubility parameters are made with the absence of any specific interactions, especially hydrogen bonds. They also do not account for the effects of morphology (crystallinity) and cross-linking. In addition, there may be (non-ideal) changes with changes in temperature and, in many cases, with changes in concentration.

Division of δ into its partial components or Hansen solubility parameters leads to the precision in the definition of likeness. Thus, liquids with similar δ_d, δ_p, and δ_h are very likely to be miscible or soluble. The method of Hoftyzer and van Krevelen (van Krevelen & Hoftyzer, 1976) estimates the individual solubility parameter components from group contributions. Another approach has been proposed by Hoy (1989) for the estimation of the solubility parameter and its components. Askadskii (2003) has used the total solubility parameter to predict the solubility of polymers in various solvents.

The difference of polymer–solvent solubility parameters are taken as a measure of mixing. In case this difference is small the idea of mixing probability is widely accepted.

$$\Delta\delta = [(\delta_{d,P} - \delta_{d,S})^2 + (\delta_{p,P} - \delta_{p,S})^2 + (\delta_{h,P} - \delta_{h,S})^2]^{1/2} \qquad (2)$$

The condition of solubility parameter difference being less than 5 is assumed to be the limit of solubility where $\Delta\delta$ is in $(J/cm^3)^{1/2}$ (van Krevelen, 1997).

Synthesis of poly(MA-*alt*-NIPA) was carried out by radical initiated solution polymerization under the given conditions. The copolymer structure was characterized by using FTIR, ^1H NMR, ^{13}C NMR, and Raman spectrophotometric methods. The ^1H NMR and ^{13}C NMR chemical shifts of poly(MA-*alt*-NIPA) were assigned and discussed. FTIR spectra of MA/NIPA copolymer indicated successful polymerization. Solubility parameters of poly(MA-*alt*-NIPA) were calculated and interactions between different polymer/solvent pairs were empirically investigated on the basis of Hoy, van Krevelen–Hoftyzer (VKH), and Askadskii’s approaches. The values obtained from the methods of Hoy and Askadskii are in good agreement with each other. The viscometric method was used to compare the correlation of the results with those obtained from algorithmic calculations.

2. Experimental

2.1. Materials

NIPA monomer (Aldrich) was purified before use by recrystallization from diethyl ether solution: b.p. 91.5 °C/2 mm, m.p. 61.6 °C. MA monomer (Fluka) was purified by recrystallization from anhydrous benzene and sublimation in vacuum: m.p. 52.8 °C. $\alpha,\acute{\alpha}$-azobisisobutyronitrile (AIBN) (Fluka) was twice recrystallized from methanol: m.p. 102.5 °C. Ethanol (EtOH), dimethylformamide (DMF), dimethylsulfoxide (DMSO), and tetrahydrofuran (THF) were used as solvent in viscometric studies.

2.2. Copolymerization

The copolymerization of MA with NIPA using monomer feed ratio MA:NIPA = 60:40 was carried out in 1,4-dioxane at 65 °C with AIBN radical initiator at constant total concentration of monomers under nitrogen atmosphere. Reaction conditions for system: $[M]_{total} = 2.78$ mol/l, $[AIBN] = 6.5 \times 10^{-3}$ mol/l.

2.3. Measurements

Raman spectra of samples were recorded using Labram 800 HR Raman spectrometer (Jobin Yvon) with a He–Ne Laser source emitting at 633 nm, 600–1200 grooves/mm holographic grating and a charge coupled device (CCD) detector. Raman spectra were obtained in 250 s integrations with an average of three scans. Spectra were recorded with reproducibility within 1 cm^{-1}. Hole: 400 μm. Resolution: 0.1 μm.

Fourier transform infrared (FTIR) spectra of KBr pellets of the samples prepared in both solvents were taken by Mattson 1000 FTIR spectrophotometer in the 4000–400 cm^{-1} range, where 40 scans were taken at 16 cm^{-1} resolution.

The microstructure of the copolymers was investigated by NMR using a Bruker 400 MHz Ultrashield spectrometer. Spectra were recorded in a deuterated DMSO.

Intrinsic viscosities of the copolymer were determined in EtOH, DMF, DMSO, THF at 20 ± 0.1 °C in the concentration range of 0.8–3.0 g/dl by Ubbelohde viscometer.

The calculated solubility parameters of the copolymer were obtained from their chemical structures of repeating units by using the explained methods of van Krevelen–Hoftyzer pair, Hoy, and Askadskii.

3. Results and discussion

3.1. Alternating copolymerization

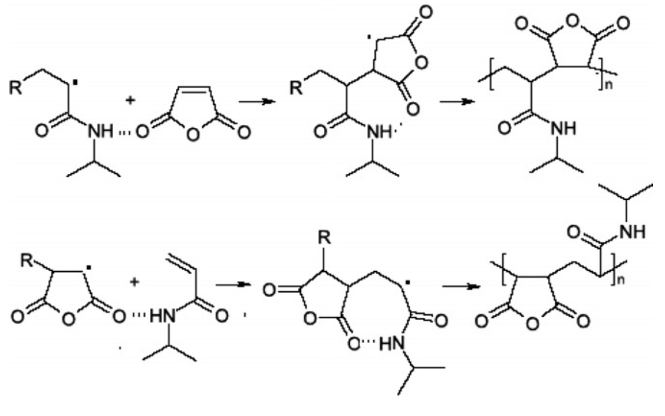
Alternating copolymerization for MA/NIPA monomer pair was achieved by Dinçer, Köseli, Kesim, Rzaev, and Pişkin (2002). Carrying out the synthesis of copolymers at five different initial monomer ratios and by the evaluation of monomer reactivity ratios, the initial monomer ratio for the alternating copolymerization was determined.

Studies show that the obtained copolymers of MA/VP (maleic anhydride/vinyl pyrrolidone) monomer pair consist of equimolar amounts of the two comonomer units, which are alternatingly arranged along the macromolecular length. Such a copolymer is formed independent of the initial ratio of the comonomers (Nagasawa & Rice, 1960). The dominating tendency toward alternation is due to the charge-transfer complex (CTC) of MA and VP (Kokubo, Iwatzuki, & Jamashita, 1968; Nikolev, 1973), which takes part in the reaction process as an independent monomer. The complex is attached to the growing polymer chain anticipated with respect to the free MA and VP, due to the affinity of CTC which is the greatest toward the growing radical (Georgiev, Konstantinov, & Kabaivanov, 1992).

In the case of copolymerization of MA with NIPA, although both MA and NIPA monomers can be considered as electron acceptors, these monomers have great tendency towards alternating copolymerization. This was explained by the effect of H-bond complex formation between C=O (anhydride) and NH (amide) groups during chain growth reactions (Dinçer et al., 2002). This effect can be illustrated as follows (Scheme 1):

The H NMR analysis data of poly(MA-*alt*-NIPA) copolymers synthesized using different monomer feed ratios are presented in Table 1 (Dinçer et al., 2002). Using these values, parameters of Kelen Tüdos (KT) equation were calculated and the results are presented in Table 2 (Dinçer et al., 2002).

As evidenced from these values, alternating copolymerization of MA with NIPA was realized by using the given monomer feed ratio and conditions. In the alternating copolymerization process of MA the monomer feed ratio was selected as 60:40.



Scheme 1. H-bonding effect in alternating copolymerization of MA with NIPA during chain growth reactions.

Table 1
^{1}H NMR analysis data for determining the composition of poly(MA-*co*-NIPA) synthesized from various initial monomer mixtures (Dinçer et al., 2002)

Monomer feed (mol%)		Am$_1$ (NIPA unit)[a]	Am$_2$ (MA unit)[a]
[NIPA]	[MA]		
70	30	0.104	0.050
60	40	0.035	0.025
50	50	0.065	0.049
40	60	0.016	0.014
30	70	0.021	0.022

[a] Integral area for CH chemical shift of NIPA (isopropyl group) and MA anhydride (methyl group) units.

Table 2
Radical-initiated copolymerization of NIPA (M_1) with MA (M_2) (Dinçer et al., 2002)

Monomer ratio F	By ^{1}H NMR f	Parameters of KT equation		
		$F^2/f+\alpha$[b]	η[a]	ξ[a]
NIPA/MA				
2.33	2.08	3.31	0.37	0.79
1.50	1.40	2.31	0.19	0.70
1.00	1.33	1.45	0.17	0.52
0.67	1.14	1.09	0.08	0.36
0.43	0.95	0.89	−0.02	0.21

Reaction conditions: solvent: 1,4-dioxane, $[M]_{total} = 2.78$ mol/l, $[AIBN] = 6.41 \times 10^{-3}$ mol/l, 65 ± 0.1 °C, conversion $\leqslant 10\%$.

[a] These values were calculated by using the following r_1 and r_2 values: 0.45 and 0.08 for NIPA–MA pair.

[b] α (arbitrary constant) $= \sqrt{(F^2/f)_{min}(F^2/f)_{max}} = 0.70$ for NIPA–MA.

3.2. Functional group analysis

In this study, FTIR, ^{1}H NMR, ^{13}C NMR, and Raman spectroscopic methods were used to confirm the structures of the synthesized copolymers.

Fourier transform infrared (FTIR) spectroscopy was used in the vibrational analysis of poly(MA-*alt*-NIPA). With the help of the added data and utilization of the group theory and normal coordinate analysis, we have been able to achieve a more satisfactory interpretation of the spectrum of poly(MA-*alt*-NIPA). The interpretation is based on previously reported vibrational studies of this copolymer.

The characteristic peaks of poly(MA-*alt*-NIPA) were approved by literature data. Ju, Kim, and Lee (2002) states that characteristic peaks of NIPA monomer are observed at 1617 cm^{-1} (C=C) and 1409 cm^{-1} (CH_2=) while vinyl groups are reported to appear at 995–905 cm^{-1} by Kim, Lee, Lee, and Kim (2003). These characteristic peaks have disappeared in the spectra of MA/NIPA copolymer indicating that the polymerization has taken place.

The FTIR spectrum of the synthesized alternating copolymer of MA with NIPA is characterized by the typical absorption bands for NIPA and anhydride units. The spectrum is presented in Fig. 1.

As shown in Fig. 1 the observed peaks in the spectrum of Poly(MA-*alt*-NIPA) studied in this work are as follows; NH stretching bands for secondary amide or for H-bonded OH group of acid fragments in the partially hydrolyzed anhydride units at 3503 and 3375 cm^{-1}, C—H stretching in CH, CH_2, and CH_3 at 2980 and 2938 cm^{-1}; complexed NH amide at 2564 cm^{-1}; C=O stretching bands of anhydride unit at 1727 cm^{-1}; C=O stretching of amide I band at 1690 cm^{-1} (s); NH amide II bending at 1544 cm^{-1} (s); double twist band for CH_3 at 1370 cm^{-1}; trans-amide III bending at 1227 cm^{-1} (m–w); C—O—C or C—N stretching band at 1170 and 1075 cm^{-1}; C—C stretching of main chain at 936 and 859 cm^{-1}; N—H deformation at 753 cm^{-1}; C—H bending for anhydride unit at 590–675 cm^{-1} are observed. Spectra of these polymers also contain characteristic bands for H-bonded C=O groups at 1633 cm^{-1} and H-bonded secondary amide NH group at 1544 and 1075 cm^{-1} (NH deformation of secondary amide and N—H bonded amide in NH···O=C— complex).

3.2.1. ^{1}H NMR analysis

The characteristic resonance signals of new synthesized copolymers are defined by comparing with the resonance signals of the previously synthesized copolymers. The characteristic peaks in the ^{1}H NMR spectra of the copolymer of MA and NIPA can be identified as: (1) 2H, CH_2 of backbone NIPA unit at 1.39–1.78 ppm; (2) 1H, CH of backbone of NIPA unit at 1.78–2.38 ppm; (3) 1H, NH 6.92–8.04 ppm; (4) 1H, CH in isopropyl group of NIPA unit at 3.88 ppm; (5) and (6) 6H, CH_3 two methyl groups of NIPA unit at 0.78–1.39 ppm; (7) and (8) 2H, CH for maleic unit 4.17 ppm (Dinçer et al., 2002).

As can be seen from Fig. 2 the characteristic peaks in the ^{1}H NMR spectra of the copolymer of MA and NIPA can be identified as: (1) 2H, CH_2 of backbone NIPA unit at 1.2–1.5 ppm; (2) 1H, CH of backbone of NIPA unit at 1.78–2.38 ppm; (3) 1H NH 7.7–8.0 ppm; (4) 1H, CH in isopropyl group of NIPA unit at 3.5 ppm; (5) and (6) 6H, CH_3 two methyl groups of NIPA unit at 0.7–1.4 ppm; (7) and (8) 2H, CH for maleic unit 4.15 ppm. The peaks at 3.4 and 2.5 ppm belong to DMSO and water, respectively. The signals obtained from the ^{1}H NMR spectra of the synthesized MA/NIPA copolymer verify the formation of

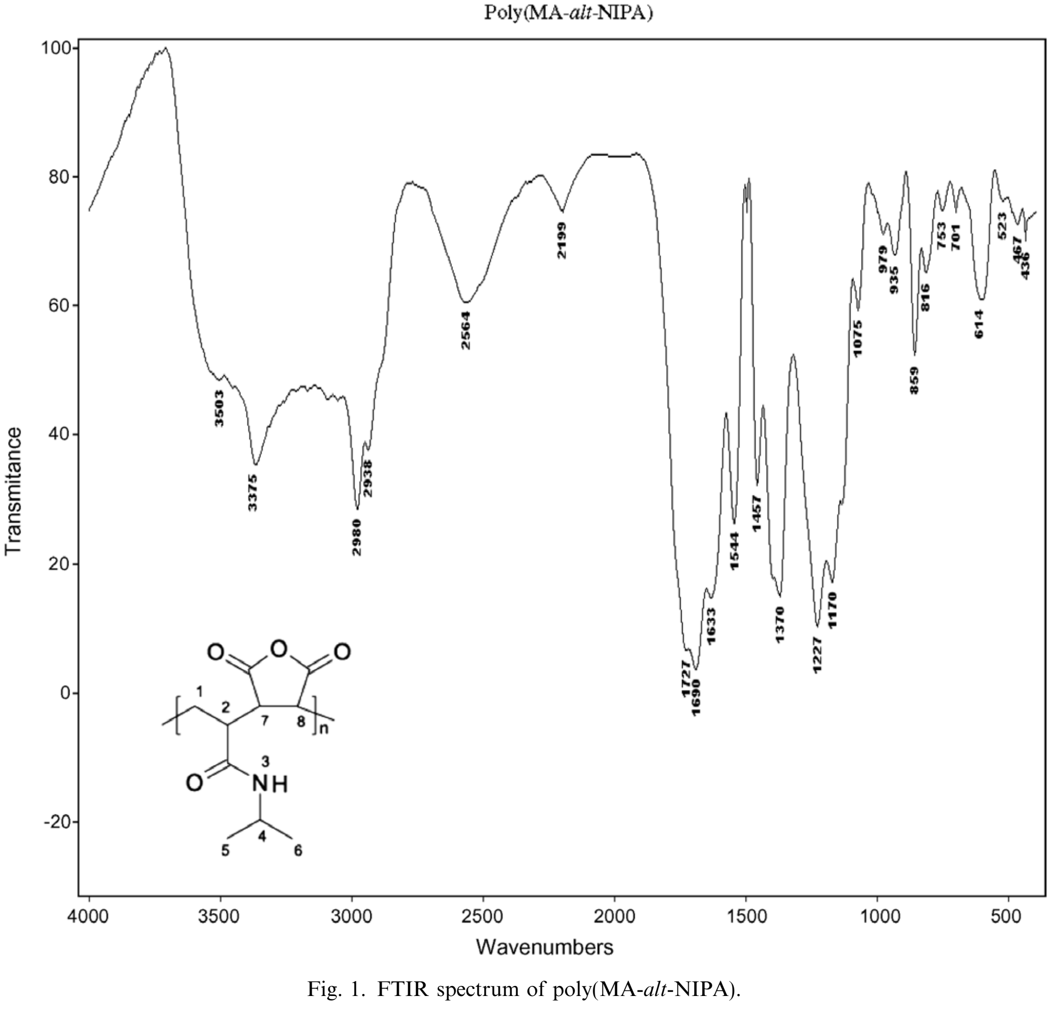


Fig. 1. FTIR spectrum of poly(MA-*alt*-NIPA).

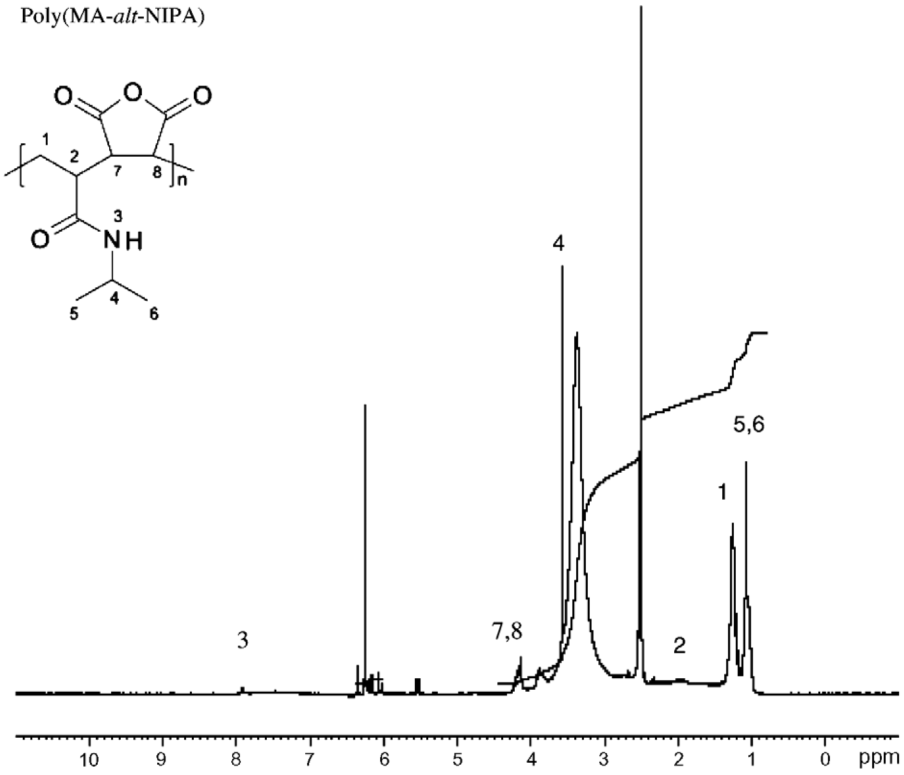


Fig. 2. ^{1}H NMR spectrum of poly(MA-*alt*-NIPA).

copolymer which are in accordance with the literature values.

3.2.2. ^{13}C NMR analysis

The structure of the copolymer was also confirmed by using ^{13}C NMR analysis. ^{13}C NMR spectrum of poly(MA-*alt*-NIPA) copolymer is given in Fig. 3.

^{13}C NMR spectrum of poly(MA-*alt*-NIPA) can be characterized by: single peak at 167.97 ppm which is coming from carbon atoms of C=O groups in both NIPA and MA units, peak appears in the range of 39.3–41.6 ppm for methylene backbone carbon (C1) (relatively broad peak), methine backbone signal for NIPA unit (C2) at 67.63 ppm and the carbon signals for two methyl groups (C5, C6) of NIPA unit at 23.61 ppm as a single peak, 40.4 ppm for CH in isopropyl group (C4), 41.7 ppm for C7 and C8 for backbone MA unit CH. Kesim, Rzaev, Dinçer, and Pişkin (2003) also reported the values for MA/NIPA. These values are in good agreement with the values obtained from present study.

3.2.3. Raman analysis

FT-Raman spectroscopy is a technique which provides structural information that is complementary to that obtained from FTIR. It has to be taken into account, however, that some of the groups show also bands in the Raman spectra, even if they are of lower intensity, and that same groups are more active in Raman than in IR. In this study, the characteristic group frequencies of Raman spectroscopy have been tabulated. The band assignments were made according to the standard spectroscopy literature (Dollish, Fateley, & Bentley, 1974) and by considering results of previous Raman studies of certain similar structures.

Raman spectra of MA/NIPA copolymer is shown in Fig. 4. Detailed peak assignments of the main absorption bands are listed in Table 3. The Raman spectra for poly(MA-*alt*-NIPA) displays characteristic absorption bands of MA and NIPA units. The characteristic C=C vibrations for maleic anhydride are at around 3111 cm^{-1} [ν(=C—H)], 1850 cm^{-1} [$\nu_{\text{symmetric}}$(C=O)], 1780 cm^{-1} [$\nu_{\text{asymmetric}}$(C=O)], 1590 cm^{-1} [ν (C=C)], 1060 cm^{-1} [$\nu_{\text{asymmetric}}$(C—O—C)], and 636 cm^{-1} [γ(=CH—H)] (Rocks, Rintoul, Vohwinkel, & George, 2004). In the corresponding Raman frequencies of VP, the carbonyl stretching vibration appeared at 1694 cm^{-1} and the carbon double bond at 1629 cm^{-1}; in the case of polymer the carbonyl frequency was found at lower frequencies (Száraz & Forsling, 2000). Polymerization can be monitored by the disappearance of the characteristic C=C vibrations from maleic anhydride (3111,1590, 636 cm^{-1}). In the Fig. 4 it can be clearly seen that those peaks have completely disappeared.

3.3. Algorithmic calculations for the determination of the solubility profile of poly(MA-alt-NIPA)

The solubility parameter of poly(MA-*alt*-NIPA) has been calculated with regard to the methods of Hoy, van Krevelen–Hoftyzer, and Askadskii.

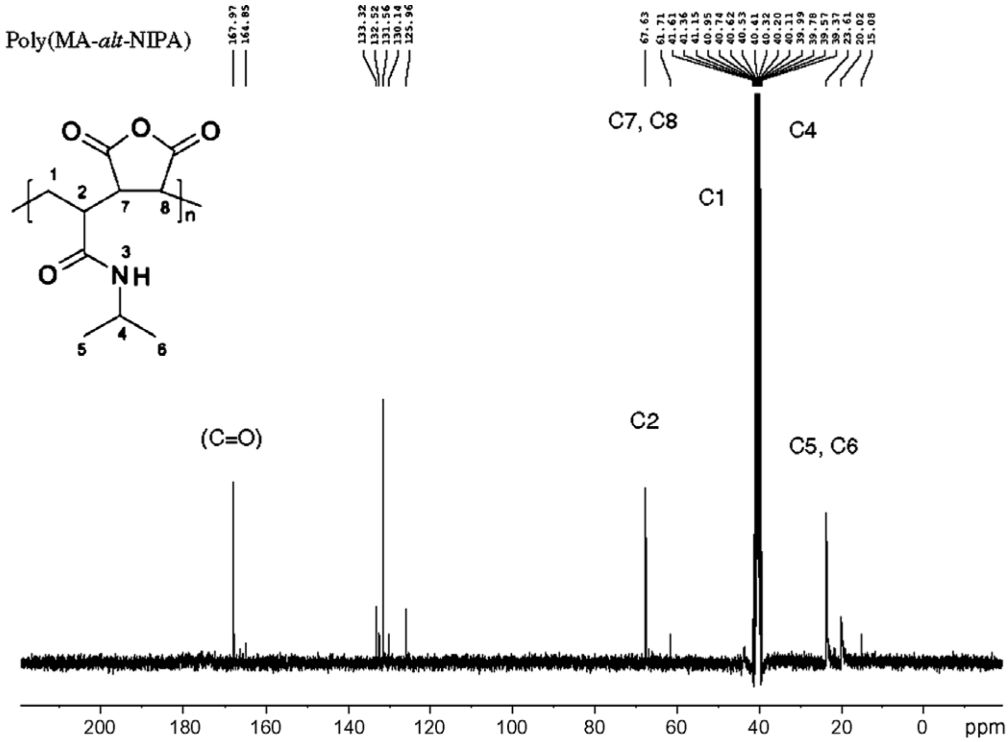


Fig. 3. ^{13}C NMR spectrum of poly(MA-*alt*-NIPA).

The main advantage of group contribution methods is that it is easy to estimate individual contributions such as dispersive (δ_d), polar (δ_p), and hydrogen bonding (δ_h) of polymers/low molecular weight compounds, through which the overall solubility parameter (δ_t) can be estimated. In many instances, the physical properties of polymers are found to correlate strongly with interconnections between the atoms of a molecule. Over the years the partial solubility parameters were determined for an enormous number of substances and lead to critical compilations as a most valuable source of information for the nature of the substances and their interactions (Barton, 1983, 1985; Hansen, 1999). The solubility parameter values were calculated by applying the dispersion and polar components of the molar attraction constant (F_{di} and F_{pi}) and contribution of the H-bonding forces to the cohesive energy (E_{hi}) of the specific groups present in the structures of the studied copolymers for the method of VKH (van Krevelen, 1997) and molar volume values derived by Fedors (1974).

By using the methods of van Krevelen–Hoftyzer (VKH), Hoy, and Askadskii, the solubility parameter (δ_t) and its components (δ_p, δ_d, δ_h) were calculated for Poly(MA-*alt*-NIPA) by using the tabulated group contributions and the calculated parameters are displayed in Tables 4 and 5.

According to VKH approach, total solubility parameter determined with regard to the solubility parameter components of poly(MA-*alt*-NIPA) is found as 31.4. The total solubility parameters and solubility parameter components calculated with regard to Hoy is found as 25.7. Considering the significance of the results obtained from both methods one can most naively state that the results of the two approaches do not differ much from each other.

Another approach in the calculation of solubility parameter is carried out by Askadskii method (2003). The total solubility parameter has been evaluated by using Askadskii's method given in Table 5, which yields a value of 27.3 for δ_t. As can be seen from Table 5, calculated δ_t value of poly(MA-*alt*-NIPA) indicates that calculated values according to Askadskii and Hoy methods are much more in agreement with each other.

The solubility behavior of a polymer depends mainly on the structure of the polymer and the interactions of solvent and polymer. It has been assumed for a long time that the like must dissolve in the like.

The poly(MA-*alt*-NIPA)/solvent systems were employed for parameters on the basis of solubility parameter with regard to the theoretical methods of Hoy, VKH, and Askadskii. There is a generally accepted rule that for a good solubility, the solubility parameters of both solvent and polymer must be close to each other. Various approaches have been developed for evaluating the solubility parameter values contributing from polymer and solvent pair individually. One of these methods is the calculation of $\Delta\delta$ values. For a good solubility $\Delta\delta$ should be small ($\leqslant 5$).

The solubility parameter components of selected 10 solvents are reported in the literature with respect to Hoy and Hansen (Barton, 1991; Brandrup & Immergut, 1989).

$\Delta\delta$ values were calculated by using both the Hoy's system and the van Krevelen–Hoftyzer's system employing Hansen's and Hoy's solubility parameter components for

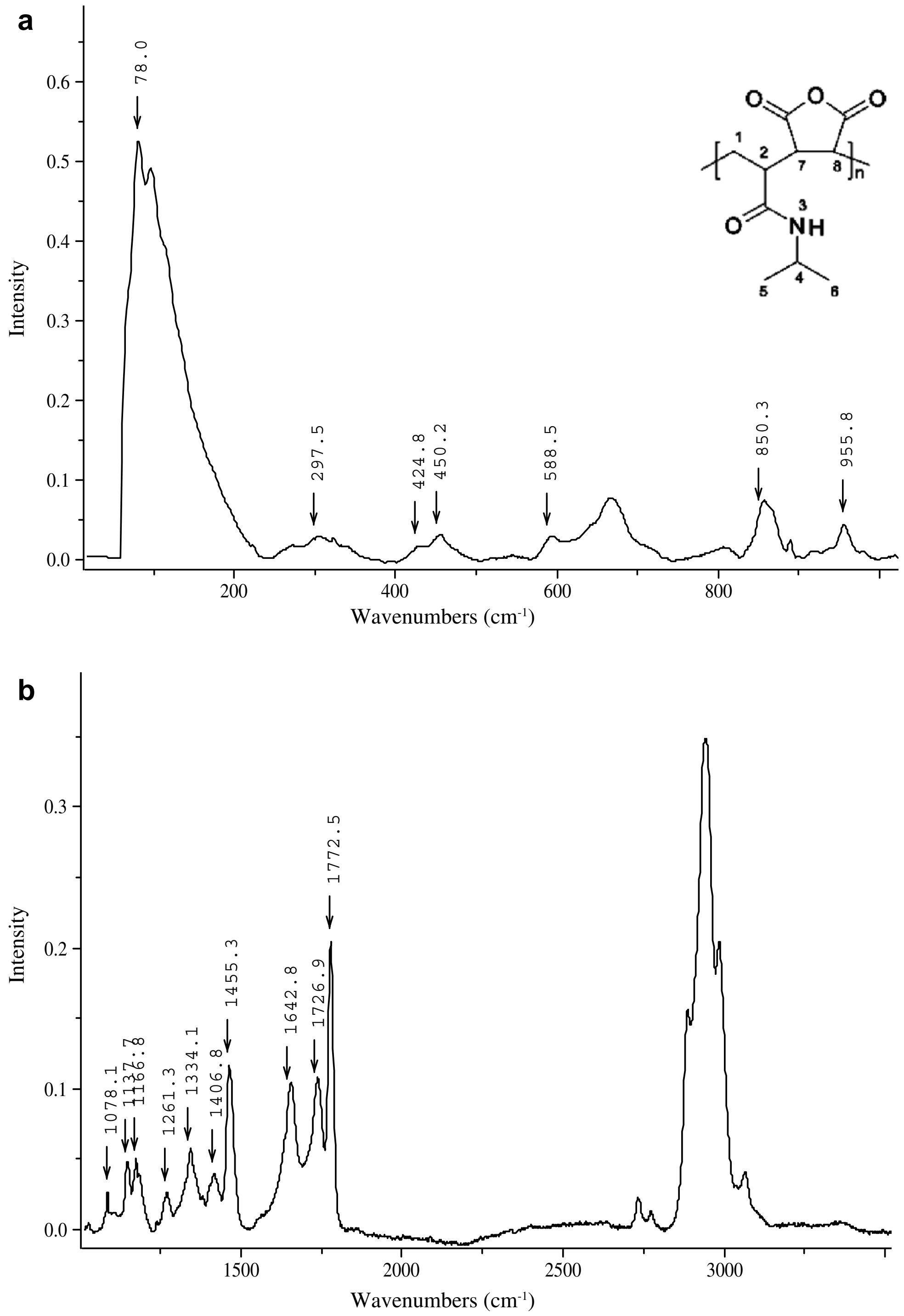


Fig. 4. Raman spectra of poly(MA-*alt*-NIPA); (a) 0–1000 cm^{-1}; (b) 1000–4000 cm^{-1}.

solvents (Barton, 1991; Brandrup & Immergut, 1989) and the results were displayed in Tables 6 and 7 for poly(MA-*alt*-NIPA) in related solvents.

According to the above calculations a sequence has been obtained for the solvent power for poly(MA-*alt*-NIPA) determined on the basis of $\Delta\delta$ values given in Table 8.

As can be seen from the tabulated values, water gives one of the highest $\Delta\delta$ values (much greater than the predicted value of 5 considered for good solubility) for this copolymer although it seems to be water soluble due to its nature. This confusion will be discussed in further parts.

3.4. Solubility diagrams

Solubility behavior cannot be accurately predicted by only the Hildebrand solubility parameter (δ). As mentioned before, solubility can be affected by any specific interactions, especially H-bonds, temperature, polymer morphol-

Table 3
Characterization of Raman bands for poly(MA-*alt*-NIPA)

Vibration frequency (cm^{-1})	Relative intensity	Mode
78.0	s	C—O, rotation; CCO, angle bending (Bailey & Koleske, 1976)
238	w	C—O, internal rotations (Bailey & Koleske, 1976); C—O—C, bending
297.5	w	C—O—C, in plane bending
424.8	w	C—O—C, symmetric deformation
450.2	w	C—C=O, in plane deformation
538	w	C—O—C, in plane bending
588.5	w	CH_2, rocking
850.3	m	C—O—C, symmetric stretching
955.8	w	CH_2, rocking; C—C, stretching
1078.1[a]	w	C—O—C, asymmetric stretching
1137.7[b]	w	C—O—C, asymmetric stretching
1166.8	w	CH_2, rock for isopropyl
1261.3	w	CH_2, twisting; N—H stretch amide III, trans, associated form
1334.1	w	CH_2, wagging; N—H stretch amide III, cis, associated form
1455.3	m–w	CH_2, scissoring; N—H stretch amide II, cis, associated form
1642.8	m–w	N—H stretch amide I, trans, cis, associated form; C=O stretching for NVP (*N*-vinyl pyrrolidone)
1726.9	m–w	C=O stretching of MA unit
1772.5	m	C=O asymmetric stretching of MA unit

s, strong; m, medium; w, weak.

[a] Intermolecular H-bonding (Morssli et al., 1991.

[b] Intramolecular H-bonding (Morssli et al., 1991).

Table 4
Calculated solubility parameter and its components for poly(MA-*alt*-NIPA) according to VKH and Hoy methods

Polymer	δ_p		δ_d		δ_h		δ_t	
	VKH	Hoy	VKH	Hoy	VKH	Hoy	VKH	Hoy
Poly(MA-NIPA)	19.6	16.2	22.9	15.4	9.0	12.8	31.4	25.7

Table 5
Calculated physical characteristics of poly(MA-*alt*-NIPA) according to Askadskii's method

Polymer	ΔE_i^* (J/mol)	ΔV_i^* (Å^3)	$\delta_t(J/cm^3)^{1/2}$
Poly(MA-*alt*-NIPA)	89450.3	199.9	27.3

Table 6
$\Delta\delta$ values for different poly(MA-*alt*-NIPA)/related solvent systems by using Hoy's solubility parameter components of solvents

System	$\Delta\delta$ $(J/cm^3)^{1/2}$	
	van Krevelen–Hoftyzer	Hoy
DMSO/poly(MA-*alt*-NIPA)	4.7	4.0
DMF/poly(MA-*alt*-NIPA)	6.6	3.5
THF/poly(MA-*alt*-NIPA)	11.4	8.3
1-Butanol/poly(MA-*alt*-NIPA)	12.1	6.7
Ethyl acetate/poly(MA-*alt*-NIPA)	12.4	8.7
1-Pentanol/poly(MA-*alt*-NIPA)	12.4	7.3
Chloroform/poly(MA-*alt*-NIPA)	12.6	8.8
EtOH/poly(MA-*alt*-NIPA)	14.9	9.2
MeOH/poly(MA-*alt*-NIPA)	19.1	12.2
Ethyleneglycol/poly(MA-*alt*-NIPA)	24.5	17.8
Water/poly(MA-*alt*-NIPA)	33.7	28.6

Table 7
$\Delta\delta$ values for different poly(MA-*alt*-NIPA)/related solvent systems by using Hansen's solubility parameter components of solvents

System	$\Delta\delta$ $(J/cm^3)^{1/2}$	
	van Krevelen–Hoftyzer	Hoy
DMSO/poly(MA-*alt*-NIPA)	3.6	3.3
DMF/poly(MA-*alt*-NIPA)	5.2	2.0
THF/poly(MA-*alt*-NIPA)	11.0	9.8
Ethyl acetate/poly(MA-*alt*-NIPA)	11.9	10.4
1-Butanol/poly(MA-*alt*-NIPA)	13.2	10.1
1-Pentanol/poly(MA-*alt*-NIPA)	13.3	10.6
Chloroform/poly(MA-*alt*-NIPA)	13.4	13.2
EtOH/poly(MA-*alt*-NIPA)	13.7	9.9
MeOH/poly(MA-*alt*-NIPA)	15.2	11.1
Ethyleneglycol/poly(MA-*alt*-NIPA)	18.2	15.0
Water/poly(MA-*alt*-NIPA)	33.9	30.8

ogy (crystallinity), and cross-linking. Also of importance is the size and shape of the polymer and solvent molecules. Therefore, several graphing and modeling techniques have been developed to aid in the prediction of polymer solubility (Burke, 1984). These solubility parameter diagrams give a quick insight to the decomposition of polymers by solvents, namely, the swelling of three-dimensional network structures by solvents, solvent crazing and cracking and the decrease in mechanical properties like tensile strength.

The use of measurable physical quantities besides the solubility parameter for expressing the solvent properties of a liquid was used by Beerbower, Kaye, and Pattison (1967), who expressed the amount of hydrogen bonding energy by the hydrogen bonding number, Δv. Beerbower et al. (1967) plotted the data for various solvents in a diagram with the solubility parameter δ along the horizontal axis and the hydrogen bonding number, Δv, along the vertical axis. All the solvents in which a given polymer is soluble fall within a certain region. Crowley, Teague, and Lowe (1966, 1967) used an extension of this method by including the dipole moment of the solvent in the characterization. However, as this involves a comparison of a number of solvents in a three-dimensional system, the method is impractical.

For practical applications a two-dimensional method is to be preferred. Thermodynamic considerations led Bagley, Nelson, and Scigliano (1971) to the conclusion that the effects of δ_d and δ_p show close similarity, while the effect of δ_h is of a quite different nature. Accordingly, they introduced the parameter $\delta_v = \sqrt{(\delta_d^2 + \delta_p^2)}$. This leads to a diagram in which δ_v and δ_h are plotted on the axes.

Other two-dimensional methods for the representation of solubility data are $\delta_p - \delta_h$ the diagram proposed by Henry (1974) and the $\delta - \delta_h$ or the $\delta - \delta_a$ diagram proposed by Hoernschemeyer (1974).

Table 8
Sequence of solvents for poly(MA-*alt*-NIPA) according to $\Delta\delta$ values

	Sequence of solvents	Calculation method	
a	DMSO > DMF > THF > 1-Butanol > Ethyl acetate = 1-Pentanol > Chloroform > EtOH > MeOH > Ethyleneglycol > Water	$\delta_{\text{polymer;VKH}}$	$\delta_{\text{solvent;Hoy}}$
b	DMSO > DMF > THF > Ethyl acetate > 1-Butanol > 1-Pentanol > Chloroform > EtOH > MeOH > Ethyleneglycol > Water	$\delta_{\text{polymer;VKH}}$	$\delta_{\text{solvent;Hansen}}$
c	DMF > DMSO > 1-Butanol > 1-Pentanol > THF > Ethyl acetate > Chloroform > EtOH > MeOH > Ethyleneglycol > Water	$\delta_{\text{polymer;Hoy}}$	$\delta_{\text{solvent;Hoy}}$
d	DMF > DMSO > THF > EtOH > 1-Butanol > Ethyl acetate > 1-Pentanol > MeOH > Chloroform > Ethyleneglycol > Water	$\delta_{\text{polymer;Hoy}}$	$\delta_{\text{solvent;Hansen}}$

a, The sequence of solvent power obtained by using the VKH method for solubility parameter of the polymer whereas for the solvents according to Hoy's values. b, The sequence of solvent power obtained by using the VKH method for solubility parameter of the polymer whereas for the solvents according to Hansen's values. c, The sequence of solvent power obtained by using the Hoy's method for solubility parameter of the polymer whereas for the solvents according to Hoy's values. d, The sequence of solvents power obtained by using the Hoy's method for solubility parameter of the polymer whereas for the solvents according to Hansen's values.

The different combinations are all derived from the basic scheme:

$$\delta^2 = \mathrlap{\overbrace{}^{\delta_v^2}}\delta_d^2 + \mathrlap{\underbrace{}_{\delta_a^2}}\delta_p^2 + \delta_h^2$$

At the moment $\delta_v - \delta_h$ the diagram seems to be the most efficient way to represent polymer–solvent interactions. Table 9 shows the axes of the diagrams proposed by Bagley et al. (1971), Henry (1974), and Hoernschemeyer (1974).

All these diagrams have a common feature such that the solubility parameter component of polymer is placed as the center of the circle. The solubility parameter components of solvents remaining within the circle and closer to the solubility parameter component of the polymer are all considered as good solvents whereas the one remaining outside the circle may be assumed as either slightly swelling the polymer or having no effect at all (Kaplan-Can et al., 2006; Özdemir & Güner, 2007).

With respect to the solubility parameter components variously chosen as the axes of these plots, the diagrams are presented in Fig. 5. When these diagrams are examined, a sequence is obtained in the order with respect to the solvent and with regard to the distance of the solubility parameter components of the solvent from the center of the circle.

Regarding to the distance of the solubility parameter components of the solvent from the center of the circles, the sequences of the solvents for poly(MA-*alt*-NIPA) are summarized in Table 10 according to Bagley et al. (1971), Henry (1974), and Hoernschemeyer (1974) diagrams.

Table 9
The coordinates of two-dimensional diagrams

Specified by	Coordinates and combinations
Bagley et al. (1971)	$\delta_v - \delta_h, [\delta_v = (\delta_d^2 + \delta_p^2)^{1/2}]$
Henry (1974)	$\delta_p - \delta_h$
Hoernschemeyer (1974)	$\delta_t - \delta_h, [\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2}]$ and $\delta_t - \delta_a, [\delta_a = (\delta_p^2 + \delta_h^2)^{1/2}]$

3.5. Askadskii's method for predicting polymer solubility

Askadskii (2003) has used the total solubility parameter to predict the solubility of polymers in various solvents. Taking into account the nature of molecules in liquids and polymers leads to the following equation for calculating the solubility parameter:

$$\delta_t^2 = \frac{\Delta E^*}{N_A \sum_i \Delta V_i} = \frac{\sum_i \Delta E_i^*}{N_A \sum_i \Delta V_i^*} \tag{3}$$

where $\Delta E^* = k\Delta E_0$ is the cohesive energy of the liquid or repeat unit of the polymer, reduced by the number of times by which the van der Waals volume of the molecule (or unit); k is the coefficient of molecular packing of the liquid or polymer. N_A is taken as $6.023 \times 10^{23}\ \text{mol}^{-1}$, ΔE_i^* is expressed in J/mol, ΔV_i in (Å^3), and δ_t in $(\text{J/cm}^3)^{1/2}$. The value of ΔE^* is additive and is represented as $\Delta E^* = \sum_i \Delta E_i^*$, where ΔE_i^* is the contribution of each atom and type of intermolecular interaction to ΔE^*. Values $\sum_i \Delta E_i^*$ for different atoms and types of intermolecular interaction.

For copolymers, the equation for calculating the solubility parameter is presented in the form:

$$\delta^2 = \frac{\alpha_1\left(\sum_i \Delta E_i^*\right)_1 + \alpha_2\left(\sum_i \Delta E_i^*\right)_2 + \cdots + \alpha_n\left(\sum_i \Delta E_i^*\right)_n}{N_A\left[\alpha_1\left(\sum_i \Delta V_i\right)_1 + \alpha_2\left(\sum_i \Delta V_i\right)_2 + \cdots + \alpha_n\left(\sum_i \Delta V_i\right)_n\right]} \tag{4}$$

where $\alpha_1, \alpha_2, \ldots, \alpha_n$ are the molar parts of the components $1, 2, \ldots, n$; $(\sum_i \Delta V_i)_n, (\sum_i \Delta V_i)_2, \ldots, (\sum_i \Delta V_i)_n$ are the van der Waals volumes of the components $1, 2, \ldots, n$; $(\sum_i \Delta E_i^*)_1, (\sum_i \Delta E_i^*)_2, \ldots, (\sum_i \Delta E_i^*)_n$ are cohesive energies of components $1, 2, \ldots, n$; N_A is the Avogadro number.

Askadskii's solubility criterion is given below:

$$\mu < 2\rho\phi\left(\phi - \sqrt{\phi^2 - 1 + a'}\right) \tag{5}$$

where ρ is constant ($2\rho = 1.374$), δ_p and δ_s are the Askadskii's solubility parameter for the polymer and solvent, respectively,

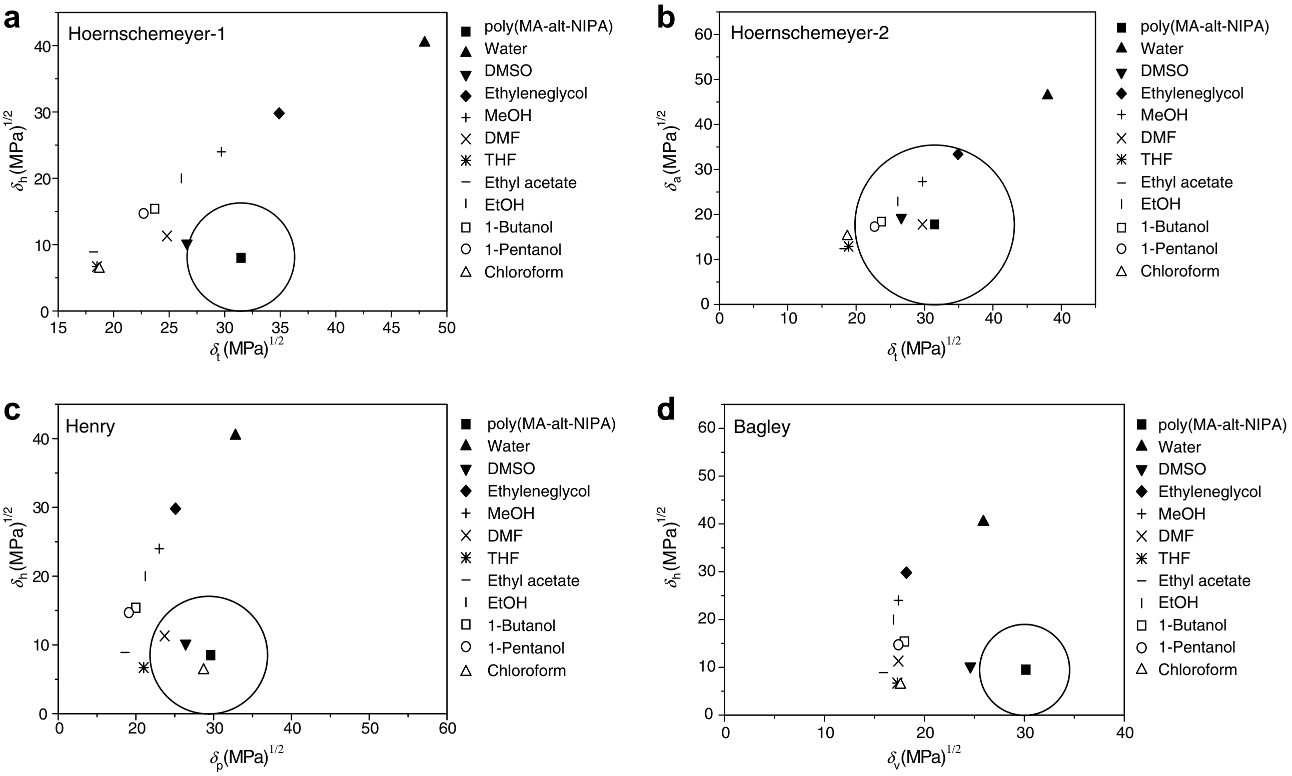


Fig. 5. (a) Solubility diagram according to Hoernschemeyer-1; (b) solubility diagram according to Hoernschemeyer-2; (c) solubility diagram according to Henry; (d) solubility diagram according to Bagley.

Table 10
The sequences of solvents for poly(MA-*alt*-NIPA) according to different solubility diagrams

Used diagram	Poly(MA-*alt*-NIPA)
Bagley	DMSO > DMF > chloroform ≈ 1-butanol > THF ≈ 1-pentanol > EtOH ≈ ethyl acetate > MeOH > ethyleneglycol > water
Henry	Chloroform > DMSO > DMF > THF > ethyl acetate ≈ 1-butanol > 1-pentanol > EtOH > MeOH > ethyleneglycol > water
Hoernschemeyer-1	DMSO > DMF > 1-butanol > EtOH > 1-pentanol > MeOH > ethyleneglycol > chloroform > THF > ethyl acetate > water
Hoernschemeyer-2	DMF > DMSO > EtOH > MeOH > 1-butanol > 1-pentanol > ethyleneglycol > chloroform ≈ THF > ethyl acetate > water

$$\phi = \frac{4(V_s V_p)^{1/3}}{(V_s^{1/3} + V_p^{1/3})^2} \tag{6}$$

$$\mu = \gamma_p^2/\gamma_s^2 \quad \text{or} \quad \mu = \delta_p^2/\delta_s^2 \tag{7}$$

Table 11 presents the calculated values of physical characteristics of related solvents and the results of the application of Askadskii's solubility criterion showing whether poly(MA-*alt*-NIPA) is soluble or not in those solvents.

After the evaluation of solubility parameter calculations and obtaining the solvent sequence, it is possible to say that DMSO was found as the best, whereas water as a poor solvent for the polymer according to Hoy and van Krevelen–Hoftyzer methods. On the other hand, according to Askadskii's method water seems to be a good solvent for poly(MA-*alt*-NIPA) besides DMSO. In theory, water and DMSO, both being polar in nature are good solvents for the copolymer having highly polar groups. At first sight, the behavior of water exhibiting large $\Delta\delta$ value seems to be confusing for poly(MA-*alt*-NIPA) which is thought to be a water-soluble polymer by the jugging of the copolymer's nature. But in the experimental part, it is understood that in practice the copolymer is not soluble in water.

In algorithmic calculations, Karger, Synder, and Eon (1976) reported that, for polymers with hydrogen bonding groups, there exists two more solubility parameter components such as acidic (δ_a) and basic (δ_b) contributions to solubility parameter besides dipole (δ_d), polar (δ_p) and hydrogen bonding (δ_h) contributions. The values of (δ_a) and (δ_b) which represent the acidic and basic characteristics (in Lewis sense) have not been reported until now. Their knowledge would provide a more realistic picture of polymer–solvent interactions, because hydrogen bonding is only possible between a proton donor and a proton acceptor-molecules.

In our study, viscosity studies have been carried out with the purpose of comparing the accordance of the results with those obtained from algorithmic calculations. The vis-

Table 11
Calculated physical characteristics of related solvents and the results of the application of Askadskii's solubility criterion for poly(MA-*alt*-NIPA)

Solvent	$\delta_{\text{solv.}}$	$V_{\text{m,solv.}}$	$\gamma_{\text{solv.}}$	L.H.S. of Eq. (2.23)	R.H.S. of Eq. (2.23)	Solubility
Water	48.14	18.0	65.39	0.329	0.775	+
DMSO	27.25	71.3	52.95	0.501	1.117	+
Ethylene glycol	25.24	56.0	27.35	1.879	0.954	–
MeOH	30.21	40.4	33.03	1.288	0.999	–
Ethyl acetate	18.44	97.8	26.50	2.001	1.047	–
EtOH	26.56	54.0	29.02	1.669	0.989	–
1-Butanol	23.09	91.7	25.84	2.105	1.016	–
1-Pentanol	22.11	108.2	25.15	2.222	1.020	–
DMF	25.94	77.0	29.92	1.570	1.097	–

L.H.S. and R.H.S. refer to left and right hand sides, respectively.

cometric studies were achieved in EtOH, DMF, DMSO, and THF as solvents. In the selection of these solvents, the algorithmic calculations have been a valuable guide. It is purposed to select good and moderate solvents for viscosity studies. DMF and DMSO appear to be good solvents for polymer systems. During the dissolution process of the copolymers, alcohol seems to be less effective in dissolving the polymer whereas water takes place in the last row.

The viscosity behavior of poly(MA-*alt*-NIPA) in the selected solvents are displayed in Fig. 6. For the selected solvents, the concentration range of the polymer solution is displayed for determining the linear behavior of the copolymer. For the copolymer system linear behavior is observed above 1.23, 0.52, 0.62, and 0.62 g/dl in EtOH, DMF, DMSO, and THF, respectively.

The larger values of $[\eta]$ imply that the polymer–solvent interactions are stronger (Barsbay & Güner, 2007). The viscosity values obtained from Huggins and Kraemer equations are in good agreement with each other, which yield DMSO as the best solvent (Table 12) due to the highest intrinsic viscosity value. These results are also consistent with those obtained from algorithmic calculations where DMSO proves to be the best solvent. Water has not been employed since great solubility problems arise and thus is replaced by THF. Our copolymer is a dibasic polyacid and its solubility in H_2O is mainly due to the functional groups, mainly, dicarboxyl groups. Thus, although the copolymer seems to be soluble in H_2O practically, when algorithmic calculations are considered H_2O proves to be a poor solvent controversially for the copolymer.

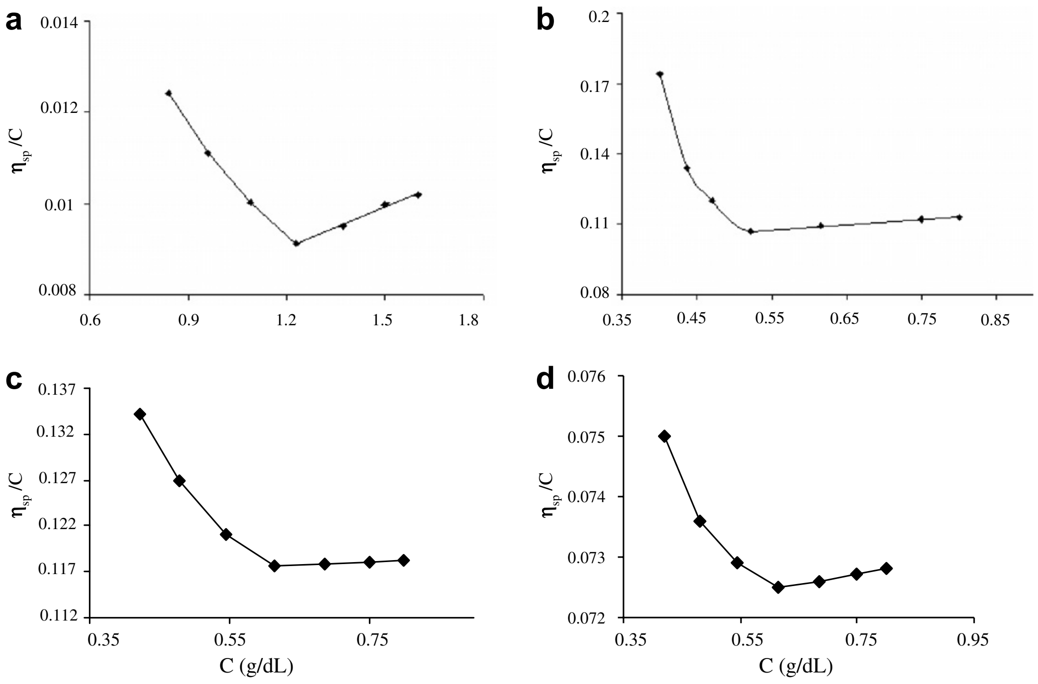


Fig. 6. (a) The reduced viscosity η_{sp}/C vs. concentration for poly(MA-*alt*-NIPA) in EtOH at 20 °C (Dilution effect and polyelectrolyte behavior). (b) The reduced viscosity η_{sp}/C vs. concentration for poly(MA-*alt*-NIPA) in DMF at 20 °C (Dilution effect and polyelectrolyte behavior). (c) The reduced viscosity η_{sp}/C vs. concentration for poly(MA-*alt*-NIPA) in DMSO at 20 °C (Dilution effect and polyelectrolyte behavior). (d) The reduced viscosity η_{sp}/C vs. concentration for poly(MA-*alt*-NIPA) in THF at 20 °C (Dilution effect and polyelectrolyte behavior).

Table 12
The linear and polyelectrolyte behavior characterizations in terms of intrinsic viscosity for poly(MA-*alt*-NIPA)/solvent system and the values of Huggins coefficient, k_H

Solvent	Concentration (g/dl)		$[\eta]_H$ (dl/g)	$[\eta]_K$ (dl/g)	k_H
EtOH	>1.23	Linear	0.005	0.006	3.34
DMF	>0.52	Linear	0.096	0.097	2.31
DMSO	>0.62	Linear	0.116	0.116	0.26
THF	>0.62	Linear	0.072	0.071	0.31

$[\eta]_H$, intrinsic viscosity obtained by applying Huggins equation; $[\eta]_K$, intrinsic viscosity obtained by applying Kraemer equation.

The behavior of polyelectrolytes in aqueous solutions show some peculiarities due to the modifications appearing probably due to the competition between the electrostatic repulsion between the polymer chain sequences carrying electric charges (Fuoss & Strauss, 1948; Katchalsky & Gillis, 1949). The maleic anhydride (MA) copolymers are usually hydrolyzed in aqueous solutions when two carboxyl groups are formed on the MA unit which results in a behavior, characteristic to dibasic polyacids. Increase in viscosity with a dilution of copolymer solution, which can be explained by specific behavior of complexed macromolecules and their conformational changes resulting in the expansion of polymer coil in diluted solution. Similar effect is not observed for the copolymers containing relatively high concentrations of MA-units due to their rigid structure and stronger intramolecular interaction inside macromolecular coils. The polyelectrolyte character can be made evident by means of viscometric measurements (Fig. 6).

The Huggins constants have been obtained for the copolymer system in each solvent and the numerical values (Table 12) strongly prove the solvent power of DMSO once again. Since the smallest k_H value has been obtained for this solvent, the interaction with the copolymer and the selected solvent is the greatest one therefore DMSO is a good solvent.

4. Conclusion

Synthesis of poly(MA-*alt*-NIPA) was carried out by radical initiated solution polymerization under the given conditions. Relatively high activity of studied MA/NIPA monomers, having tendency towards alternating copolymerization, was explained by the effect of H-bond formation between C=O (anhydride) and NH (amide) groups during chain growth reactions.

The copolymer structures were characterized by using FTIR, ^{1}H NMR, ^{13}C NMR, and Raman spectrophotometric methods. The ^{1}H NMR and ^{13}C NMR chemical shifts of poly(MA-*alt*-NIPA) were assigned and discussed. FTIR spectra of MA/NIPA copolymer indicated successful polymerization.

Solubility parameters of poly(MA-*alt*-NIPA) were calculated and interactions between different polymer/solvent pairs were empirically investigated on the basis of Hoy, van Krevelen–Hoftyzer, and Askadskii's approaches. $\delta_t$values of the copolymers were determined by Hoy, van Krevelen–Hoftyzer, and Askadskii's methods. The values obtained from the methods of Hoy and Askadskii are in good agreement with each other.

With regard to the total solubility parameter values, and concerning Askadskii's approach, DMSO and water appear to be the best solvents for MA/NIPA copolymer. On the other hand, according to Hoy and van Krevelen–Hoftyzer approaches and on the basis of solubility parameter differences ($\Delta\delta$), DMSO appears to be the best solvent whereas water is a poor solvent for the copolymer. As a consequence of the evaluation of solubility parameter diagrams, for poly(MA-*alt*-NIPA) copolymer, DMSO is sometimes replaced by DMF and chloroform. However, it is most probable to conclude that DMSO is usually the best solvent among all other solvents employed in this study.

The viscometric method was used to compare the correlation of the results with those obtained from algorithmic calculations. Interactions and behavior of poly(MA-*alt*-NIPA) were investigated by using EtOH, DMF, DMSO, THF as solvents. Starting with the classical Huggins equation, intrinsic viscosities of copolymer/solvent pairs were determined which provided a valuable information to remark the effect of solvent power on the copolymers. These solvent systems represented polyelectrolyte behavior. Consequently, the evaluation of intrinsic viscosity values implies that DMSO proves to be the best solvent for poly(MA-*alt*-NIPA) copolymer due to the highest intrinsic viscosity value.

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