H-Bonding Effect in Radical Terpolymerization of Maleic anhydride, Acrylic acid (Methyl acrylate) and Vinyl acetate

Maleik Anhidrit, Akrilik Asit (Metil Akrilat) ve Vinil Asetat Terpolimerizasyonunda H-bağı Etkisi

Research Article

Hatice Kaplan Can[1],*, Zakir MO Rzayev[2], Ali Güner[1]

[1] Hacettepe University, Faculty of Science, Department of Chemistry, Polymer Chemistry Division, Beytepe, Ankara, Turkey.

[2] Hacettepe University, Institute of Science & Engineering, Division of Nanotechnology & Nanomedicine, Beytepe, Ankara, Turkey

ABSTRACT

The ternary copolymerization of vinyl acetate (VA), maleic anhydride (MA) and acrylic acid (AA) or methylacrylate (MAc as a model comonomer), considered as donor–acceptor–acceptor systems, was carried out in p-dioxane in the presence of benzoyl peroxide (BPO) as initiator in nitrogen atmosphere at 70°C. Constants of copolymerization and complex formation for the monomer systems studied were determined by the Kelen-Tüdös, UV(H-complex) and ^{1}H-NMR (CTC, charge transfer complex) methods, respectively. Analogous H-complex effect is evidenced from comparison of copolymerization of both MA–AA (H-complex) and MA–MAc binary systems in which are realized alternating and random copolymerization, respectively. Hydrolyzed VA–MA–AA terpolymers with different composition containing regular H-complexed fragments in side-chain of macromolecules are displayed different thermal properties, including glass-transition and melting (crystalline phase) behaviors, depending on content of H-bonding fragment. Structural peculiarities (FTIR analysis) and structure-thermal properties (DSC and TGA analyses) and crystalline (X-ray diffraction analysis) relationship of terpolymers synthesized are also discussed.

Key Words

Copolymerization, terpolymerization, H-complex, charge transfer complex, structure-property relationship, thermal properties.

ÖZET

Vinil asetat (VA), Maleik Anhidrit (MA) ve Akrilik Asit (AA) veya Metil akrilat (MAc, model komonomer) alıcı-verici-alıcı sisteminde; benzoil peroksit (BPO) başlatıcısı varlığında p-dioksan içerisinde azot atmosferinde 70°C'de üçlü kopolimerizasyon gerçekleştirilmiştir. Kopolimerizasyona ait sabitler ve monomer sistemlerinin oluşturduğu kompleks oluşumu Kelen-Tüdös, UV (H-kompleksi) ve ^{1}H-NMR (CTC, Yük Transfer Kompleksi) yöntemleri kullanılarak belirlenmiştir. MA-AA (H-kompleksi) ve MA-MAc sistemlerinin ardışık ve gelişigüzel ikili kopolimerizasyon oluşumunda H-kompleksinin etkisi karşılaştırma yapılarak açıklanabilmektedir. Makromolekülün yan gruplarında, düzenli H-kompleksi içeren hidroliz olmuş farklı kompozisyonlara sahip VA-MA-AA terpolimeri; H-bağının içeriğine bağlı olarak, camsı geçiş sıcaklığı ve erime sıcaklığı (kristal faz) gibi farklı ısısal özellikler gösterirler. Sentezlenen terpolimerlerin yapısal farklılıkları (FTIR analizi), yapı-ısısal özellikleri (DSC ve TGA analizleri) ve kristal özellikleri (XRD analizi) tartışılmıştır.

Anahtar Kelimeler

Kopolimerizasyon, Terpolimerizasyon, H-kompleksi, Yük transfer kompleksi, Yapı-özellik ilişkileri, Isısal özellikler.

Article History: Received June 27, 2012; Revised July 10, 2012; Accepted August 3, 2012; Avaliable Online: August 17, 2012.

Correspondence to: Hatice Kaplan Can, Hacettepe University, Faculty of Science, Department of Chemistry, Polymer Chemistry Division, Beytepe, Ankara, Turkey

Tel: +90 312 297 60 81 Fax: +90 312 299 21 63 E-Mail: hkaplan@hacettepe.edu.tr

INTRODUCTION

It is well known that H-bonding as a variety of intermolecular interaction exert essentially influenced on kinetic and elementary actions of radical polymerization. Thermodynamic peculiarities of H-complex formation in the monomer-monomer and monomer-solvent systems were described by Kabanov, *et al.*[1,2] Hydrogen bonding is one of the important non-covalent interactions in nature[3]. The bonding energies for normal hydrogen bonds are between 10 and 50 kJ/mol. These stable and dynamic molecular complexes can be prepared by simple molecular self-assembly processes using such hydrogen [4]. H-bond is formed due to both electrostatic[3] and donor-acceptor interactions in H-complexes [5-6]. Despite that considerable contribution of an electrostatic interaction to energy of H-bond role of charge transfer (donor-acceptor interaction), which is reasonable for change of electron state and reactivity of individual components of monomer H-complex system, is highly essential. Thus, change of electron structure of 2- and 4-vinylpyridines, dimers of unsaturated carbonic acids and amides with formation of H-complexes was confirmed by IR and NMR-spectroscopy.[2] In these systems, anomaly high shifts and broad of H-bond in IR spectra and its high chemical shifts of proton in NMR spectra were observed. It is demonstrated that the formation of H-complexes of (metha)acrilic acids with some N-containing monomers (amides of unsaturated carbonic acids, N-vinylcarbazole, vinylpyrrolidone, etc.) is accompanied by essential change of copolymerization constants and parameters of *Q* and *e* mainly due to change of polarization sign of monomer double bonds. It was proposed that the unsaturated carbonic acids and amides in the dimer forms with the resonance structures should be characterized by higher energy of stabilization of double bound as compared with monomer forms of these systems.[2] This phenomenon was studied in detail by Kerber and Hlaman.[7] It was shown that dimers dissociated in solvent, capable of H-bond formation, and were substituted with H-complexes of acids with solvent. Equilibrium constants (4-6 l mol $^{-1}$) for organic acid-solvent complexes were determined by cryoscopy and IR-spectroscopy methods.[3] It was also shown that equilibrium constant of dimerization of acrylic acid in the inert solvents was 360 L mol^{-1}. As evidenced from this value, full shift of equilibrium in side of dimer formation takes place in the acrylic acid—non-polar solvent system.

The determination of self-association and inter-association equilibrium constants of H-bond formation has been discussed in detail by Coleman, *et al.*[8-11] According to authors H-bonds are dynamic, continually breaking and reforming under the influence of thermal motion, and there exists at any instant of time a distribution of species consisting of "free" (non-hydrogen bonded) monomers, hydrogen bonded dimers and hydrogen bonded multimers ("chain-like" trimers, tetramers, etc.). Naturally, this distribution is affected by changes in temperature and concentration. The IR spectral bands at 3630, 3530 and 3350 cm^{-1} have been assigned to non-hydrogen bonded OH groups, hydrogen bonded OH dimers and hydrogen bonded multimers, respectively. This spectral information forms the basis for the determination of equilibrium constants and enthalpy of hydrogen bond formation that describe the self-association of low molar mass molecules.[5]

Effect H-complex in radical alternating copolymerization of MA and fumaric acid (FA) with acrylic acid (AA) was observed by El'Said, *et al* [12] They are showed that copolymerization of these monomer pairs proceeds through formation of MA…AA and FA…AA H-complexes (—C=O…HO—) and it is possible to direct of process away from formation of alternating copolymers to formation of random copolymers with different composition by using naphthalene as a electron donor substance forming donor-acceptor complex with double bond of acceptor MA. Analogous effect was observed in copolymerization of methacrylic acid with maleic acid in water at different pH[1,8].

Semchikov, *et al*[12]. were found that an addition of solvent, which was formed H-complex with acrylic acids, decreased acid contents in their copolymers with MMA and styrene. In the both monomer systems, increase of r_1 value and decrease of r_2 value was observed. These changes were related with decreasing resonance stabilization monomers (*Q* parameter). In the case of radical copolymerization of trialkylstannyl methacrylates with maleic anhydride an effect alternation also observed which is explained by change of double bond conjugation allowing a transfer of methacrylic monomers from electron-acceptor state to electron-donor character. This effect is realized due to formation of coordination complexes between comonomers or free monomer and growing radicals through $-R_3Sn\ldots O=C-$ bond.[13-15] Analogous alternating effect were observed for radical copolymerization of carbonyl- and nitrile-containing monomers in the presence of complexing agents of Lewis acid type.[16]

The various approaches to the problem of solvent effect were reviewed and discussed.[17-23] In specific cases it is necessary to consider the formation of a CTC between the solvent and one solute and this can be accounted for by considering competing equilibrium and calculating separate K_c values for both monomer...solvent and monomer... monomer complexes. Polar and electrostatic solvent effects on reactivities of vinyl monomers were considered by Plochocka in detail.[24] Monomer CTCs as the active intermediate parts in radical copolymerizations are also interacted with solvent used in reaction. A solvent may also interfere in the propagation step via complexation with the monomer. The use of monomer-monomer CTCs to explain deviations from the terminal model was first suggested by Bartlett and Nozaki, later developed by Seiner and Litt, and refined by Cais, *et al*.[26] It was proposed that two monomers could form a 1:1 complex and be added to the growing chain as a single unit in either direction. Recently Coote, *et al*.[27] reviewed and discussed the main known mechanisms by which the solvent (which may be one or both of the comonomers) can affect the propagation kinetics of free-radical copolymerization reactions including (1) polarity effect, (2) radical-solvent complexes, (3) monomer-solvent complexes, and (4) bootstrap effect. Toppet, *et al*.[15] showed that in the case of transfer from acrylic acid(AA)–styrene(St) copolymerization in bulk to copolymerization in DMF, change of copolymer composition accompanied by change of monomer units distribution, which was different from those ones calculated according to statistical model of Markov chain of 1-order. As followed from ^{13}C-NMR study of these authors, macromolecular chains of copolymer had more length AA unit fragments as compared with those calculated using known constants of copolymerization for AA and tyrenes pair (r_1 = 0.05 and r_1 = 1.6). Although this anomaly observed was insufficiently explained by authors, nevertheless, there was well witnessed that the mechanism of copolymerization, indeed, was more complicated than mechanism proposed in accordance with classical Mayo-Lewis scheme.

Recently we have reported that H-complex formed in the maleic anhydride-acrylic acid system plays an important role in radical terpolymerization of donor-acceptor monomers.[28] The objective of the present work is to study the radical terpolymerization of vinyl acetate (VA)–maleic anhydride (MA)–acrylic acid (AA) or and VA–MA–MAc (methyl acrylate as a model third monomer non forming H-complex) electron donor-electron acceptor and proton acceptor-proton donor monomer systems and structure and thermal properties such as melting, glass-transition and destruction behaviors of polyfunctional H-bonded macromolecules.

EXPERIMENTAL

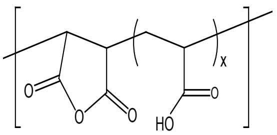
Materials

VA, AA, and MAc (Fluka) were distilled before use. They had the following average characteristics: VA, bp 72.5°C, d_4^{20} 0.9315, n_D^{20} 1.3950; AA, bp 141.6°C, mp 13.5°C, d_4^{20} 1.0510, n_D^{20} 1.4215; MAc, bp 79°C, d_4^{20} 0.9555, n_D^{20} 1.4030. MA (Fluka) was purified before use by recrystallization from anhydrous benzene and by sublimation in vacuo, mp. 52.8°C. Benzoyl peroxide (BP, Fluka) was purified by recrystallizing twice from chloroform solution by methanol when was dried under vacuum, mp.106°C. Other reagents including organic solvents were purified by ordinary methods.

Copolymerization

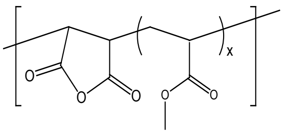
Copolymerization of MA with AA and MAc, as well as terpolymerization of VA, MA and AA or MAc were carried out in similar conditions, in *p*-dioxane in the presence of BP (0.1 %) as an initiator at 70°C under a nitrogen atmosphere. The MA–AA (or MAc) copolymers and VA–MA–AA (or MAc) terpolymers were isolated from the reaction mixture by reprecipitation with anhydrous methanol and *n*-hexane, respectively. Copolymers were purified by twice reprecipitating from dioxane solution with *n*-hexane and by washing with several portions of hexane, benzene and diethyl ether, and were dried *in vacuo* at 50°C to a constant weight with almost quantitative yields (~75 %). Terpolymers were purified by several reprecipitating from anhydrous acetone solution with hexane and by washing with hexane and benzene, and were dried *in vacuo* at 60°C to a constant weight with quantitative yields (~95 %). The copolymers and terpolymers synthesized by the use of 1 : 1 and 1 : 2 : 1 molar ratios of initial monomers, respectively, had following characteristics:

Poly(MA-alt-AA) Copolymer



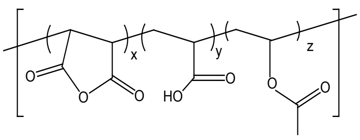
where x=1.12 (AA unit=52.83) yield 80 %, glass transition temperature T_g 111°C and T_m 153°C (by DSC analysis), intrinsic viscosity $[\eta]_{in}$ in *p*-dioxane at 25°C 1.25 dlg^{-1} , acid number AN= 878 mg KOH/g, monomer unit ratio in copolymer (m_1:m_2)= 1:1.12.

Poly(MA-ran-MAc) copolymer



where x=3.5 (MAc unit= 60.47) yield 87 % , glass transition temperature T_g 120 °C and T_m 167 °C (by DSC analysis), intrinsic viscosity $[\eta]_{in}$ in *p*-dioxane at 25°C 0.27 dlg^{-1}, acid number AN=572 mg KOH/g.

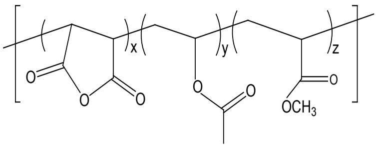
Poly(AA-co-MA-co-VA)terpolymer



where x, y ,z (MA unit= 45.15 –50.02 , AA unit= 15.31-20.97, VA unit=30.34 –36.36) yield 85 %, glass transition temperature T_g 146-196 °C and T_m 153-206 °C (by DSC analysis), intrinsic viscosity $[\eta]_{in}$ in *p*-dioxane at 25°C 1.36 dlg^{-1}, acid number AN=710 mg KOH/g, monomer unit ratio in copolymer (m_1:m_2:m_3)=1:2:1.

FTIR spectra (film), cm^{-1}: νOH 3060 (broad, in –COOH), νCH_3 2950 (as) and 2880 (s), νCH_2 2930 (as) and 2870 (s), νCOOH 2545 (broad), νC=O 1836 (as) and 1766 (s) (C=O in anhydride unit), νC=O 1730 (C=O in ester group), νC=O 1585 (as) (in COO$^-$), δCH_2 1478 and 1443 (doublet), δCH_3 1385 and 1357 (doublet), δC-O 1240-1170 (ester and carboxyl), νC-O-C 1035 (in anhydride unit), δOH 943 (out-of-plane OH bending), δCH 886 and 871 (doublet), δCH_3 842 (rock), δCH_2 720 (rock), δCH 645 (in main chain from anhydride unit), and δO-C=O 560 (s) (bend of COOH);

Poly(MAc-co-MA-co-VA) terpolymer



$[\eta]_{in}$ 0.32 dL/g in p- dioxane at 25°C, T_g 130.5°C and T_m 152°C (by DSC), and acid number 710 mg KOH/g;

FTIR spectra (film), cm^{-1}: νCH_3 2950 (as) and 2880 (s), νCH_2 2930 (as) and 2870 (s), νCOOH 2545 (broad), νC=O 1835 (as) and 1768 (s) (C=O in anhydride unit), νC=O 1733 (C=O in ester group), δCH_2 1454, δCH_3 1380 and 1368 (doublet), δC-O 1215-1143 (ester and carboxyl), νC-O-C 1063 (in anhydride unit), δCH 870 and 865 (doublet), δCH_3 825 (rock), δCH_2 700 (rock), δCH 645 (in main chain from anhydride unit), and δO-C=O 578 (s) (bend of ester group). In the FTIR spectra of hydrolyzed terpolymers there are disappeared characteristic bands for anhydride units, and appeared new bands in field of 1970, 1585 and 1630 cm^{-1} relating to –COOH groups, as well as increased in intensity of 3060 and 2545 cm^{-1} broad bands. These terpolymers easily are transformed to the anhydride forms after thermotreatment at 120-130°C during 15 min.

MEASUREMENTS

H-Complex formation in MA–AA monomer system was studied by UV-method using Hitachi 100-50 model UV visible double beams spectrophotometer and *p*-dioxane solutions of monomer mixtures with various monomer ratios at 20 ± 0.1°C.

Equilibrium constant of MA...AA charge transfer complex (CTC) formation was determined by ^{1}H NMR method using Bruker DPX300 NMR spectrometer with 300 MHz frequency, CH_3-CO-CH_3-d_6 and deuterated *p*-dioxane as solvent and tetramethylsilane as a internal standard at 25 ± 0.1°C.

Fourier transform infrared (FTIR) spectra of copolymer films or thin coatings on KBr pellet were recorded with FTIR Nicolet 510 spectrometer in the 4000-400 cm^{-1} range, where 30 scans were taken at 4 cm^{-1} resolution. For the composition analysis of terpolymers, specifically contents of VA and AA (or MAc) units, characteristic absorption bands of 1360 cm^{-1} (for VA unit), 1630 cm^{-1} (for MA-maleic acid units) and 1580 cm^{-1} (for AA unit) were used as analytical bands. The least changing absorption band of 1130 cm^{-1} was used as a standard band ($A = \log (I_o/I)$, $\Delta A^i = A^i/A^{1130}$) to calculate the terpolymer compositions.

The acid number (AN) of the anhydride-containing copolymers and terpolymers were determined by known non-aqueous titration method.[16]

Intrinsic viscosities of copolymers and terpolymers synthesized were determined in *p*-dioxane at 25 ± 0.1°C in the concentration range of 0.1-1.0 dlg^{-1}using an Ubbelohde viscosimeter.

Differential scanning calorimetric (DSC) and thermogravimetric (TGA) analyses of copolymers and terpolymers were carried out with a DuPont V4.1C 2000 and DuPont TA 2000 in nitrogen atmosphere at a heating rate of 5°C/min.

The powder diffraction patterns of synthesized samples were recorded using Philips manual spectrogoniometer employing CuK_α ($\lambda = 1.54184$ Å) radiation over the range $5^o \leq 2\theta \leq 50^o$Crystallinity degrees of new products were determined by area ratio method

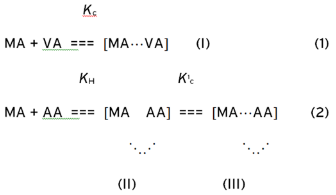
$$X_c = {}_o\int^{\infty} s^2\, I_c(s)\, ds \;/\; {}_o\int^{\infty} s^2\, I(s)\, ds$$

where s is the magnitude of the reciprocal-lattice vector and is given by $s=(2\sin\theta)/\lambda$ θ is one–half the angle of deviation of the diffracted rays from the incident X-rays, λ is the wavelength, I(s) is the intensity of coherent X-ray scatter from a specimen (both crystalline and amorphous), $I_c(s)$ is the intensity of coherent x-ray scatter from the crystalline region. In this method, the areas of amorphous and crystalline parts of the patterns were calculated.

RESULTS AND DISCUSSION

H-Bonding and Charge Transfer Complex Formations

From the structural peculiarities of monomers of ternary systems studied may be predict that the formation of the two types of intermolecular complexes, such as charge transfer complex (CTC) between double bond of MA (electron acceptor) and vinyl acetate (electron donor) and H-complex between MA (C=O, proton acceptor) and AA (COOH, proton donor) proceeds as the following:



$$MA + VA \overset{K_c}{===} [MA\cdots VA] \quad (I) \qquad (1)$$

$$MA + AA \overset{K_H}{===} \underset{(II)}{[MA\quad AA]} \overset{K'_c}{===} \underset{(III)}{[MA\cdots AA]} \qquad (2)$$

where (I) is CTC, (II) is only H-complex forming through >C=O...HOOC– bond, and (III) is CTC forming due to charge transfer from AA double bond to MA double bond which is caused by effect of H-complex between functional groups of comonomers. From known values of polarity (*e*)[22] for MA as a strong acceptor monomer (*e* = 2.25) and AA as a relatively weakly acceptor monomer (*e* = 0.77) as well as for sodium acrylate (where H is substituted with more polar Na) as an electron-donor monomer (*e* = –0.12) evidenced that the formation of H-complex in the MA–AA system can be accompanied by change of conjugation between double bond and carbonyl group and increase of electron density of acrylic double bond.

In this case H-complexed AA can by described as an electron-donor monomer. This is allowed easily electron transfer in the monomer mixtures from H-complexed AA to MA with formation of CTC between double bonds of comonomers.

Known equilibrium constant for MA…VA complex is 0.06 l mol^{-1} in $CHCl_3$ at 25°C (by UV method).[20] Formation only H-complex in the MA–AA monomer system and alternating copolymerization of this pair were observed by El'Saied, *et al.*[11] However, there does not determined constant of complex-formation for MA and AA pair. It was expressed an opinion that H-bond effect on reactivate of monomers and radicals in the main is related with redistribution of their π-electron density in H-complex on account of charge transfer type of donor-acceptor interaction.[2]

The formation of two types of complexes in the MA–AA monomer system with further determination of their K_H and K_C values were studied using UV and ^{1}H NMR spectroscopy and the following well known equations of Benesi-Hildebrand,[18] Ketelaar[19] and Hanna-Aushbaugh,[23] respectively:

$$[A].l\,/d = 1/\varepsilon_c + 1/\varepsilon_c.\,K_C.[D] \tag{3}$$

$$1/(\varepsilon_a - \varepsilon^f_{er}) = 1/\{(\varepsilon_{A\ldots D} - \varepsilon^f_{er})K_C[D]\} + 1/(\varepsilon_{A\ldots D} - \varepsilon^f_{er}) \tag{4}$$

where [A] and [D] are molar concentrations of acceptor and donor monomers, respectively, *d* is optical density, K_C equilibrium constant of complex-formation, ε_a is the apparent molar extinction of the A in the mixture, ε^f_{er} is the molar extinction of free A in pure solvent however at the wavelength of maximum absorption in pure D, and $\varepsilon_{A\ldots D}$ is the molar extinction of the complex (through –COOH…O=C< bond).

$$1/\Delta_{exp} = 1/\Delta_c + 1/(\Delta_c c).[D]^{-1} \tag{5}$$

where $\Delta_{exp} = \delta^f_{er} - \delta^c_a$ is difference between chemical shifts of free and complexed A monomer in the various mixtures with D monomer ([D]>>[A]) and Δ_c is related to chemical shift of monomer CTC.

The results obtained from UV study of MA and AA monomer mixtures at different wavelengths near maximum absorption (255-270 nm) in pure *p*-dioxane are presented in Figure 1-3 and Tables 1. Electron spectra of monomer mixtures of (*a*) MA/MAc (MAc-methyl acrylate as a model monomer) and (*b*) MA/AA are recorded at various ratios of monomer feed (Figure 1). As evidenced from comparative analysis of these spectra the values of λ_{max} almost do not change with dilution of mixture and change of monomer molar ratios in the MA–MAc system, while the essential displacement of λ_{max} (from 252 to 278 nm) is observed for the MA–AA system which is caused by substitution of dioxane…AA associates to MA…AA monomer H-complexes. Equilibrium constants (K_H) and extinction coefficients (ε) for the H-bond complexes at various λ_{max} are determined using UV spectroscopy data and corresponding equations (3) and (4) from Benesi-Hildebrand (Figure 2) and Ketelaar (Figure 3) plots, and results obtained are summarized in Table 1. As seen from these values the use of both methods allows to obtain the close results for the MA–AA system.

Known model of H-bond even if there is regard as electrostatic interaction[25] that should be also foreseen possibility and consequence of charge transfer interaction in H-complexes, i.e., formation of CTC in MA–AA monomer system between electron acceptor MA double bond and electron donor AA double bond (only in the mixtures with MA after realizing a H-complex formation). In order to confirm this acceptor-donor interaction, the ^{1}H NMR spectra of free MA and its various mixtures (MA<<AA) with AA are recorded by using NMR spectrometer with 300 MHz resolution, and results obtained are analyzed according to equation (5).

NMR spectra of MA and different MA/AA mixtures recording in two different solvents are illustrated in Figure 4 and 5, and results obtained are summarized in Table 2. The concentration of acceptor MA is constant (0.1 mol l^{-1}). The appreciable displacement of chemical shifts observed for symmetric anhydride protons (δ^f = 7.349 and 7.083 ppm in deuterated acetone and *p*-dioxane, respectively) toward higher (in acetone) and lower (in dioxane) fields at excessive amounts of donor AA monomer ($\Delta_{exp} = \delta^f - \delta^c$ = 0.011-0.039 ppm in deuterated acetone and Δ_{exp} = 0.033-0.060 ppm in deuterated dioxane) allows one to determine K_c value for MA...AA CTC from plot of 1/Δ_{exp} vs. 1/[AA] : K_c = 0.056 ± 0.003 l mol $^{-1}$ (0.051 by least squares analysis) and 0.16 ± 0.01 l mol $^{-1}$ (0.17 by least squares analysis) at 25 ± 0.1°C in deuterated acetone and *p*-dioxane, respectively. As seen from ^{1}H NMR spectra, proton of carboxyl group also is shifts (but lower fields) by increasing in AA concentration and in this case a narrowing of peak and increase of its intensity are observed. This fact can be explained by partial formation of dimer form of H-bonded carboxyl group or by increasing a fraction of AA...dioxane complex in the condition of AA>>MA. Observed relatively low value of K_c in acetone in comparison with those in *p*-dioxane can be interpreted by effect solvent through formation of complex between donor carbonyl group of acetone with acceptor double bond of MA,[20] which essentially reduces acceptor properties of MA and therefore equilibrium constant of MA...AA complex. Determination of K_H and K_c values by mentioned methods is realized in polar solvent that corresponded to the conditions of copolymerization reaction.

Complex-Radical Terpolymerization

The ternary monomer systems studied can be classified as donor (VA)–acceptor (MA)–acceptor (AA or MAc as a model monomer) systems which can be characterized as follows: (1) the acceptor–donor monomer pair of VA–MA has a tendency to the charge transfer complex-formation; (2) monomer pair of MA–AA formed H-complex and on account of change of the π-electron structure of AA monomer, its double bond knowledged donor properties; (3) MA does not homopolymerize in selected conditions of terpolymerization; (3) the formation of poly-VA and poly-AA fragments in low conversion conditions can be ignored taking

Table 1. The values of equilibrium constants (K_H) and coefficient extinction (ε) for the H-bond formation in MA (C=O, proton acceptor) – AA (proton donor) monomer system. Solvent-***p***-dioxane, 25 ± 0.1 °C, [AA] = const = 4.08.10^{-3} mol L^{-1}, [MA] >> [AA].

Parameters	By B-H equation at λ_{max} values (nm) of				By Ketelaar equation at λ_{max} values (nm) of			
	255	260	265	270	255	260	265	270
K_H (L mol $^{-1}$)	493	441	450	469	491	438	415	447
	*(528)	(431)	(462)	(478)	(477)	(440)	(410)	(450)
e_C (L mol $^{-1}$ cm^{-1})	571	481	408	328	463	437	376	307
	*(511)	(474)	(405)	(318)	(466)	(438)	(377)	(307)

* The values are calculated by least squares analysis.

Table 2. ^{1}H NMR spectra data for calculation of equilibrium constant (K_c) for CTC formation in MA–AA acceptor-donor monomer system. Solvent, deuterated acetone and ***p***-dioxane, 25 ± 0.1 °C.

[MA] (mol L^{-1})	[AA] (mol L^{-1})	*δ^{MA} (ppm)	Δ_{exp} (ppm)	1/Δ_{exp} (ppm)$^{-1}$	1/[AA] (L mol^{-1})
in deuterated acetone					
0.1	1.13	7.338	0.011	90.91	0.885
0.1	2.17	7.328	0.021	47.62	0.461
0.1	3.41	7.320	0.029	34.48	0.293
0.1	4.68	7.310	0.039	25.64	0.214
in deuterated dioxane					
0.1	3.00	7.116	0.033	30.30	0.333
0.1	4.00	7.122	0.039	25.64	0.250
0.1	5.60	7.136	0.053	18.87	0.179
0.1	10.6	7.143	0.060	16.67	0.094

* δ^{MA} = 7.349 and 7.083 ppm for symmetrical MA protons in deuterated acetone and ***p***-dioxane, respectively.

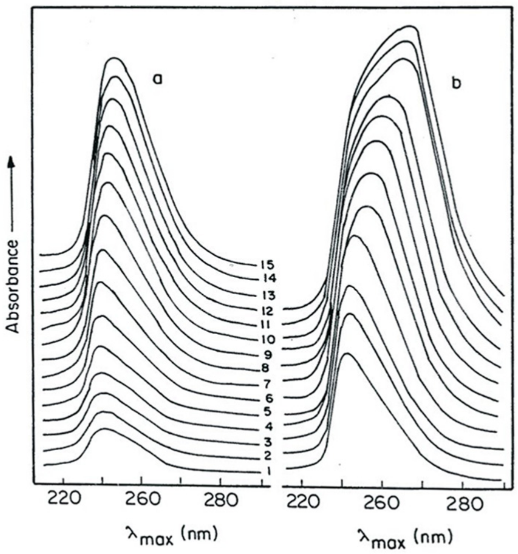


Figure 1. UV spectra of MAc (a-1), AA (b-1), MAc/MA (a:1-15) and AA/MA (b:1-12) mixtures in p-dioxane at 25 ± 0.1oC. [AA] and [MAc] = const = 4.08.10-3 mol l-1, [MA] = (4.08-0.816).10-3 mol l^{-1}.

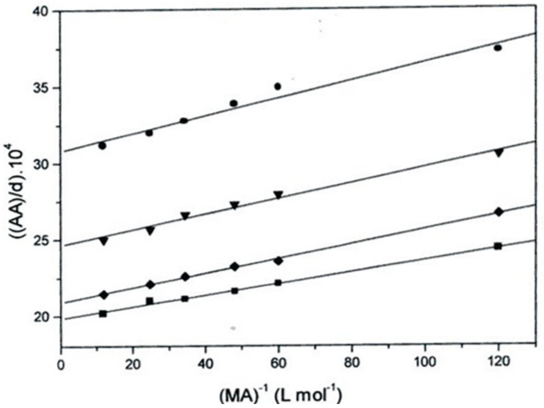


Figure 2. Benesi-Hildebrand plot of [AA]/d vs. $[MA]^{-1}$ for determining equilibrium constant (K_H) of H-bond formation in the MA (C=O, proton acceptor)-AA(COOH, proton donor) monomer system. Solvent - *p*-dioxane, 25 ± 0.1oC, λ_{max} = 255 (-●-), 260 (-▾-), 265 (-◆-) and 270 nm (-□-).

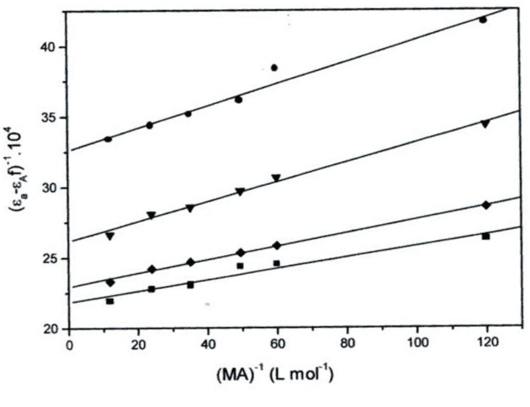


Figure 3. Ketelaar plot of $(\varepsilon_a - \varepsilon^f_A)^{-1}$ vs. $[MA]^{-1}$ for determining equilibrium constant (KH) of H-bond formation in the MA – AA monomer system. Conditions of UV measurement as in Figure 2.

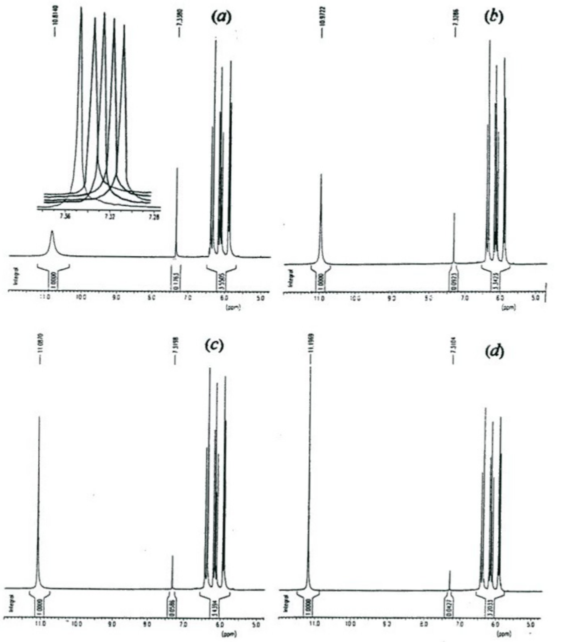


Figure 4. ^{1}H NMR spectra of MA (δ^f = 7.349 ppm) and its mixtures with AA at molar ratio of [MA] : [AA] = 1: 11.3 (a), 1: 21.7 (b), 1: 34.1 (c) and 1: 46.8 (d). Solvent-CH_3COCH_3-d_6, internal standard-tetramethylsilane, 25 ± 0.1°C.

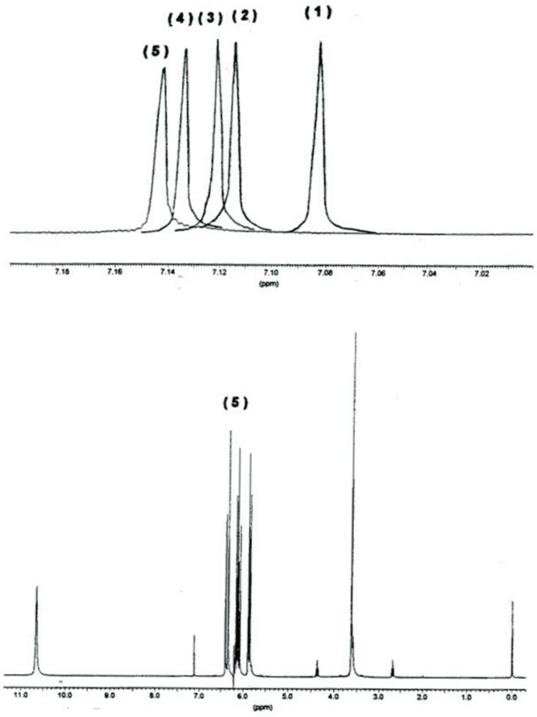


Figure 5. ^{1}H NMR spectra of MA (δ^f = 7.083 ppm) (1) and its mixtures with AA at molar ratio of [MA] : [AA] = 1: 3 (2), 1: 4 (3), 1: 5.6 (4) and 1: 10.6 (5). Solvent-deuterated p-dioxane, internal standard-tetramethylsilane, 25 ± 0.1°C.

into consideration the high reactivity of their macroradicals toward other monomers; (4) the formation of VA–AA diads can also does not take place, and in this case ~VA$^{\cdot}$ and ~AA$^{\cdot}$ growing macroradicals have lower activity toward AA and VA monomers, respectively; (5) known values of monomer reactivity ratios (r_1 and r_2) for the monomer pairs and parameters of specific activity (*Q*) and polarity (*e*) of monomers of the ternary system studied also confirmed the above suggestions:[22] $Q_1 = 0.026$ and $e_1 = -0.22$ (for VA); $Q_2 = 0.23$ and $e_2 = 2.25$ (for MA); $Q_3 = 1.15$ and $e_3 = 0.77$ (for AA); $Q_3 = 0.42$ and $e_3 = 0.60$ (for MAc); $r_{12} = 0.072$ and $r_{21} = 0.01$ (for VA–MA); $r_{13} = 0.1$ and $r_{31} = 10.0$ (for VA–AA); $r_{13} = 0.1$ and $r_{31} = 9.0$ (for VA–MAc); $r_{23} = 0.02$ and $r_{32} = 2.8$ (for MA–MAc); $r_{23} = 0.036$ and $r_{32} = 24.7$ (calculated values for MA–AA).

On the base of these selective characteristics of self-organized ternary systems, i.e., systems with H-complexed and CT-complexed monomer pairs, studied, elementary stages of propagation reactions in the condition of stationary kinetics (≤10 % conversion) can be proposed for participation of both complexed and free monomers in the following preferable initiation and chain growth reactions:

Initiation via complex-bound monomers

$$R^{\bullet} + VA\ldots MA \xrightarrow{k_i} R\text{–}VA^{\bullet}\ldots MA \rightarrow R\text{–}VA\text{–}MA^{\bullet} \qquad (6)$$

$$R^{\bullet} + VA\ldots MA \xrightarrow{k_i} R\text{–}MA^{\bullet}\ldots VA \rightarrow R\text{–}MA\text{–}VA^{\bullet} \qquad (7)$$

$$R^{\bullet} + MA\ldots AA \xrightarrow{k_i} R\text{–}MA^{\bullet}\ldots AA \rightarrow R\text{–}MA\text{–}AA^{\bullet} \qquad (8)$$

$$R^{\bullet} + MA\ldots AA \xrightarrow{k_i} R\text{–}AA^{\bullet}\ldots MA \rightarrow R\text{–}AA\text{–}MA^{\bullet} \qquad (9)$$

Initiation via free monomers

$$R^{\bullet} + VA \xrightarrow{k_i} R\text{–}VA^{\bullet} \qquad (10)$$

$$R^{\bullet} + MA \xrightarrow{k_i} R\text{–}MA^{\bullet} \qquad (11)$$

$$R^{\bullet} + AA \xrightarrow{k_i} R\text{–}AA^{\bullet} \qquad (12)$$

Chain growth via complex-bound monomers

$$\sim VA^{\bullet} + MA\ldots VA \xrightarrow{k_{1c1}} \sim VA\text{–}MA^{\bullet}\ldots VA \rightarrow \sim VA^{\bullet} \qquad (13)$$

$$\sim VA^{\bullet} + MA\ldots AA \xrightarrow{k_{1c2}} \sim VA\text{–}MA^{\bullet}\ldots AA \rightarrow \sim AA^{\bullet} \qquad (14)$$

$$\sim MA^{\bullet} + VA\ldots MA \xrightarrow{k_{2c1}} \sim MA\text{–}VA^{\bullet}\ldots MA \rightarrow \sim MA^{\bullet} \qquad (15)$$

$$\sim MA^{\bullet} + AA\ldots MA \xrightarrow{k_{2c2}} \sim MA\text{–}AA^{\bullet}\ldots MA \rightarrow \sim MA^{\bullet} \qquad (16)$$

$$\sim AA^{\bullet} + MA\ldots VA \xrightarrow{k_{3c1}} \sim AA\text{–}MA^{\bullet}\ldots VA \rightarrow \sim MA^{\bullet} \qquad (17)$$

$$\sim AA^{\bullet} + MA\ldots AA \xrightarrow{k_{3c2}} \sim AA\text{–}MA^{\bullet}\ldots AA \rightarrow \sim AA^{\bullet} \qquad (18)$$

Chain growth via free monomers

$$\sim VA^{\bullet} + MA \xrightarrow{k_{12}} \sim VA^{\bullet} \quad (19) \qquad \sim VA^{\bullet} + AA \xrightarrow{k_{13}} \sim AA^{\bullet} \quad (20)$$

$$\sim MA^{\bullet} + VA \xrightarrow{k_{21}} \sim VA^{\bullet} \quad (21) \qquad \sim MA^{\bullet} + AA \xrightarrow{k_{23}} \sim AA^{\bullet} \quad (22)$$

$$\sim AA^{\bullet} + VA \xrightarrow{k_{31}} \sim VA^{\bullet} \quad (23) \qquad \sim AA^{\bullet} + MA \xrightarrow{k_{32}} \sim MA^{\bullet} \quad (24)$$

Obviously, the participation of CT- and H-complexes in chain growth reactions will be reflected on the copolymerization rate in the initial stage and on the copolymer compositions at various initial monomer ratios. Terpolymerization reactions of VA–MA–AA ternary system were carried out in the wide range of initial monomer compositions in degassed glass tubes or dilatometers in *p*-dioxane with BP (0.2 %) as an initiator at 70°C under nitrogen atmosphere.

The terpolymers synthesized were characterized by nonaqueous titration of the free anhydride side-chain groups (acid number) as well as by FTIR spectroscopy for the determination of VA and AA unit contents. The absorption value ratios between characteristic analytical bands of 1360 cm^{-1} (for VA unit), 1630 cm^{-1} (for MA-maleic acid units) and 1580 cm^{-1} (for AA unit) and the least changing absorption

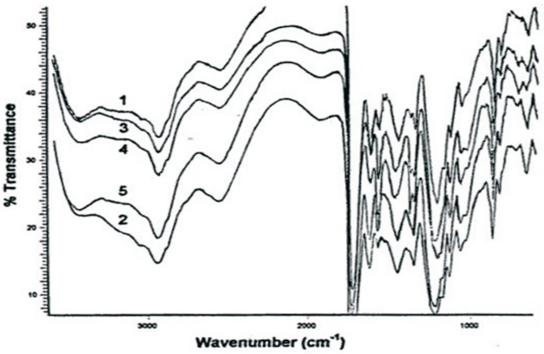


Figure 6. FTIR spectra of VA–MA–AA terpolymers preparing in different monomer feed. [VA]:[MA]:[AA] = 15:50:35 (1), 20:50:30 (2), 25:50:25 (3), 30:50:20 (4) and 35:50:15 (5).

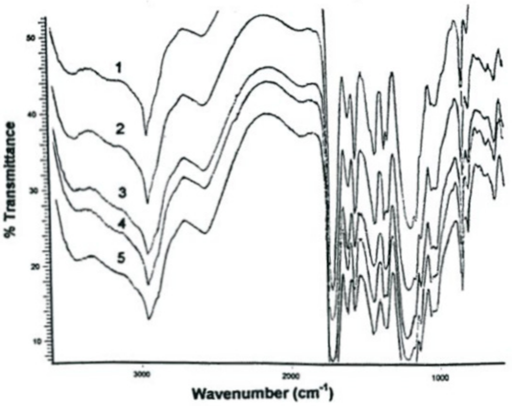


Figure 7. FTIR spectra of VA–MA–MAc terpolymers preparing in different monomer feed. [VA]:[MA]:[AA] = 20:20:60 (1), 25:25:50 (2), 30:30:40 (3), 33.3:33.3:33.4 (4), and 37.5:37.5:25 (5).

band of 1130 cm^{-1} as a standard band (A = log (I_o/I), $\Delta A^i = A^i/A^{1130}$) were used to calculate the terpolymer compositions. Molar fractions (in mol %) of comonomer units (m_1, m_2 and m_3) in VA(M_1)–MA(M_2)–AA(M_3) terpolymers using FTIR analysis data are calculated according to the following equations:

$$m_1 = \frac{\Delta A^{1360}/M_1}{\Delta A^{1360}/M_1 + \Delta A^{1630}/M_2 + \Delta A^{1580}/M_3} \cdot 100 \qquad (25)$$

$$m_2 = \frac{\Delta A^{1630}/M_2}{\Delta A^{1360}/M_1 + \Delta A^{1630}/M_2 + \Delta A^{1580}/M_3} \cdot 100 \qquad (26)$$

$$m_3 = \frac{\Delta A^{1580}/M_3}{\Delta A^{1360}/M_1 + \Delta A^{1630}/M_2 + \Delta A^{1580}/M_3} \cdot 100 \qquad (27)$$

where $m_1/m_2 = [\Delta A^{1360}/M_1]/[\Delta A^{1630}/M_2]$, $m_1/m_3 = [\Delta A^{1360}/M_1]/[\Delta A^{1580}/M_3]$, $m_2/m_3 = [\Delta A^{1630}/M_2]/[\Delta A^{1580}/M_3]$, $\Delta A = A^i / A^{1130}$ (standard band), M_1, M_2 and M_3 are molecular weights of VA, MA and AA monomer units, respectively. Results of FTIR analyses of VA–MA–AA and VA–MA–MAc (as a model system) terpolymers synthesized by using various initial monomer ratios are illustrated in Figure 6 and 7, respectively.

On the base if these data the values of absorption bands for the comonomer units are calculated which are used for the determination of terpolymer compositions according to (25) - (27) equations. The results obtained are presented in Table 3. As evidenced from these data, change of VA (donor) and AA (acceptor) concentrations in monomer feed leads to the formation of terpolymers with similar molar ratios of m_1/m_2 and m_2/m_3 monomer units.

In the analogous conditions, terpolymerization of VA, MA and Methyl acrylate (MAc) as a model system, in which is absented H-complex, is carried out. The results obtained for the both terpolymers preparing in the low conversion conditions are summarized in Tables 3-5, respectively.

A diagram of monomer-terpolymer compositions are illustrated in Figure 8. As evidenced from these results, the small change in the monomer unit ratios take place for the both ternary systems at nearly equimolar ratios of VA/MA and MA/AA monomers in poly(VA-*co*–MA-*co*–AA) system and VA/MA in poly(VA-*co*-MA-*co*-MAc) system. It is also shown that the nature of M_3 acceptor monomer (AA or MAc), as well as a change of monomer composition has strong influence on the character of diagram point distributions (Figure 8). On the other hand, in the result of binary copolymerization of equimolar mixtures of MA–AA and MA–MAc pairs in the similar reaction conditions the formations of alternating and random copolymers, respectively are observed. From the data of chemical analysis (titration of anhydride units) it is found that poly(MA-*alt*-AA) copolymer has monomer unit composition equal to m_1: m_2 = 1:1.12, while monomer unit composition of MA–MAc is 1:3.5.

On the base of these results obtained, it can be suggested that (1) binary copolymerization of

Table 3. FTIR analysis data for the determination of composition of VA–MA–AA terpolymers synthesized in the various initial monomer mixtures. Analytical absorption bands: 1360 cm^{-1} ($\nu_{C=O}$ in VA-unit), 1630 cm^{-1} ($\nu_{C=O}$ in MA-maleic acid unit), and 1580 cm^{-1} ($\nu_{C=O}$ in AA-unit).

Monomer Feed (mol %)			ΔA^{1360}	ΔA^{1630}	ΔA^{1580}	AN* (mgKOH/g)		TerpolymerComposition (% mol)		
				(in acid form)		calculated	found			
[VA]	[MA]	[AA]	(VA unit)	(MA unit)	(AAunit)			m_1	m_2	m_3
15	50	35	0.238	0.447	0.129	751.7	729.3	30.34	50.02	19.64
27	50	30	0.124	0.218	0.055	736.2	725.4	32.53	50.23	17.24
25	50	25	0.168	0.255	0.087	705.0	711.2	33.88	45.15	20.97
30	50	20	0.211	0.312	0.098	697.7	703.4	35.05	45.50	19.45
35	50	15	0.237	0.317	0.100	707.0	705.1	36.36	48.33	15.31

* These values are calculated using FTIR analysis data; for the equimolar terpolymer composition (1: 2 : 1) ***AN*** of 811 mg KOH/g is calculated.

complexed monomers (CTC and H-complex) can be realized in the poly(VA-*co*–MA-*co*–AA) ternary system, and (2) binary copolymerization of VA...MA complex with free MAc monomer will be proceeded in the poly(VA-*co*-MA-*co*-MAc) ternary system. It can by assumed that for the both ternary systems studied the reactions proceeded by complex-radical copolymerization of VA...MA (CTC) and MA...AA (H-complex) complexed monomers with formation of copolymers predominantly containing VA–MA and MA–AA alternating fragments. Therefore, to determine the relative activity of these complexed monomers, terpolymerizations were carried out under conditions that ensure complex-formation to a maximum extent: with constant concentrations of MA equal to 50 mol % (in VA–MA–AA system), equimolar ratios of VA/MA (in VA–MA–MAc system) and low conversion conditions of copolymerization (≤10 %).

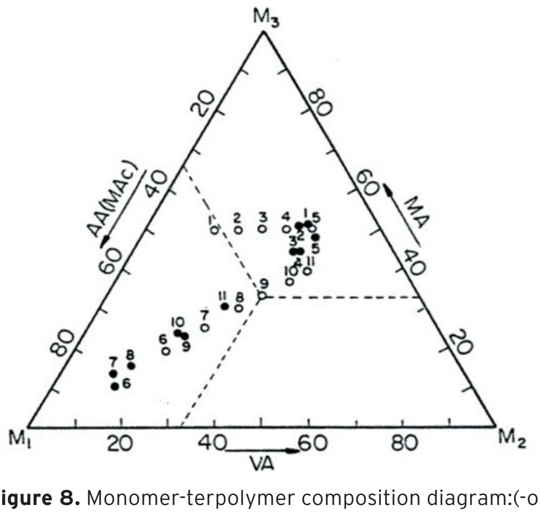


Figure 8. Monomer-terpolymer composition diagram:(-o-) for monomer and for (-•-) VA–MA–AA and (-Δ) VA–MA–MAc terpolymer compositions, respectively.

The monomer (complexomer) reactivity ratios of two CTCs for ternary system studied were determined by using of modified terminal model of Kelen-Tüdös equation [24-25] in the following form:

$$\eta = [(r_1K_1/K_2 + r_2(K_1/K_2)^{-1}/\alpha]\ \xi - r_2(K_1/K_2)^{-1}/\alpha \text{ (for VA...MA–MA...AA system)} \tag{28}$$

$$\eta = [(r_1K_1 + r_2/K_1)/\alpha]\ \xi - r_2/K_1)/\alpha \text{ (for VA...MA–MAc system)} \tag{29}$$

where $\eta = (F^2/f)/(F^2/f + \alpha)$; $\xi = [F(f-1)/f]/(F^2/f + \alpha)$; $\alpha = \sqrt{(F^2/f)_{min} . (F^2/f)_{max}}$;

K_1 and K_2 are constants of CTC formation for VA...MA and MA...AA monomer complexes, respectively; F = [VA...MA] / [MA...AA] (or [MAc]) and f = m_1 / m_2. Copolymerization constants are obtained using experimental data (Table 4 and 5) from Kelen-Tüdos plots of η vs. ξ for the both VA...MA (C_I) and MA...AA (C_{II}) and VA...MA (M_1) and MAc (M_2) pairs, respectively, as follows: $r_1 = 0.66 \pm 0.03$ and $r_2 = 0.16 \pm 0.01$ for VA...MA–MA...AA pair and $r_1 = 0.31 \pm 0.02$ and $r_2 = 2.35 \pm 0.1$ for VA...MA–MAc pair. Taking into consideration of K_1 and K_2 values obtained for VA...MA and MA...AA complexes the copolymerization constants for VA...MA–MA...AA pair change as follows: $r_1 K_1/K_2 = 0.71$ and $r_2 K_2/K_1 = 0.15$. As evidenced from the values of complexed monomer reactivity ratios complex-radical alternating terpolymerization is realized in the poly(AA-*co*-MA-*co*-VA) system at given monomer feed due to the both H-complex and charge transfer interaction effects. While an absence of H-bonding

Table 4. Copolymerization of VA…MA and MA…AA complexed monomers in the various initial monomer mixtures. Reaction conditions: Solvent (S) - ***p***-dioxane, $[M]_{total}$ = 4.4 mol L^{-1} , [S] / $[M]_{total}$ = 2.6, [BP] = $2.06.10^{-3}$ mol L^{-1}, 70°C, conversion ≤ 10 %.

Monomer Feed (mol%)		Copolymer Composition (mol %)		Parameters of KT-Equation				
$[C_I]$	$[C_{II}]$	m_I	m_{II}	F^2/f	$F(f-1)/f$	$F^2/f+\alpha$*	η	ξ
30	70	60.68	39.32	0.1193	0.1510	0.6127	0.2464	0.1947
40	60	65.06	34.94	0.2389	0.3088	0.7323	0.4217	0.3262
50	50	67.76	32.24	0.4757	0.5243	0.9691	0.5410	0.4909
60	40	70.10	29.90	0.9600	0.8600	1.4534	0.5917	0.6605
70	30	72.73	27.27	2.0408	1.4582	2.5342	0.5754	0.8053

* α (arbitrary constant) = $\sqrt{(F^2/f)_{min} \cdot (F^2/f)_{max}}$ = 0.4934.

Table 5. Copolymerization of VA–MA–MAc as a model system in the various initial monomer mixtures. Reaction conditions as in Table 4.

Monomer Feed (mol %)			AN* (mgKOH/g)	Terpolymer Composition (mol %)			Parameters of KT- Equation		
[VA]	[MA]	[MAc]		m_1	m_2	m_3	$F^2/f + \alpha^{\S}$	$\eta.10^2$	$\xi.10^2$
20	20	60	212.2	10.37	11.81	77.82	5.8374	-28.66	26.74
25	25	50	259.7	12.05	13.73	74.22	7.1558	-26.26	40.24
30	30	40	297.3	1.41	16.41	69.18	9.3269	-20.02	54.15
33.3	33.3	33.4	375.5	20.06	22.84	57.10	9.6005	-6.90	55.46
37.5	37.5	25	382.2	1.58	23.45	55.97	15.717	-5.17	72.79
40	40	20	453.9	26.99	30.74	42.27	15.992	6.70	73.26

* For the equimolar terpolymer composition (1: 1 : 1) *AN* of 415.3 mg KOH/g is calculated. $^{\S}\alpha$ = 4.276.

effect in the poly(VA-*co*-MA-*co*-MAc) system is caused realization of terpolymerization in the state nearly binary random copolymerization of VA…MA complexed monomer with free MAc monomer.

Effect of H-Complex in Structure-Thermal and Crystalline Behaviors Relationship

One of important intra- and intermolecular structural characteristics of polyfunctional polymers is structural regularity and bond flexibly of their macromolecules. When the polar polymers possess H-bonding capability, the most energetically favored crystal structures will tend to capitalize on these features.[27]

Synthesized poly(AA-*co*-MA-*co*-VA) terpolymer containing regular H-compelled fragments in side-chain of macromolecules can display different thermal properties, including melting and glass-transition behaviors, depending on content of H-bonding fragment. The results of DSC and TGA studies of terpolymers are illustrated in Figure 9-11, and are summarized in Table 6. As evidenced from these data poly(AA-*co*-MA-*co*-VA) terpolymers with different composition have characteristic glass-transition endotherms (T_g) in the field of 146.0, 153.5, 186.5 and 197.5°C, as well as different decomposition behaviors (Figure 9). A appreciable increase T_g values with decreasing acid number values from 725 to 703 mgKOH/g is observed. Similarly melting temperature (T_m) changes and moreover, intensity of endotherm is decreased by shift of T_m to higher temperature region. This seems to be related to the crystalline phase which is formed through intermolecular H-bonding between free –COOH group containing functional

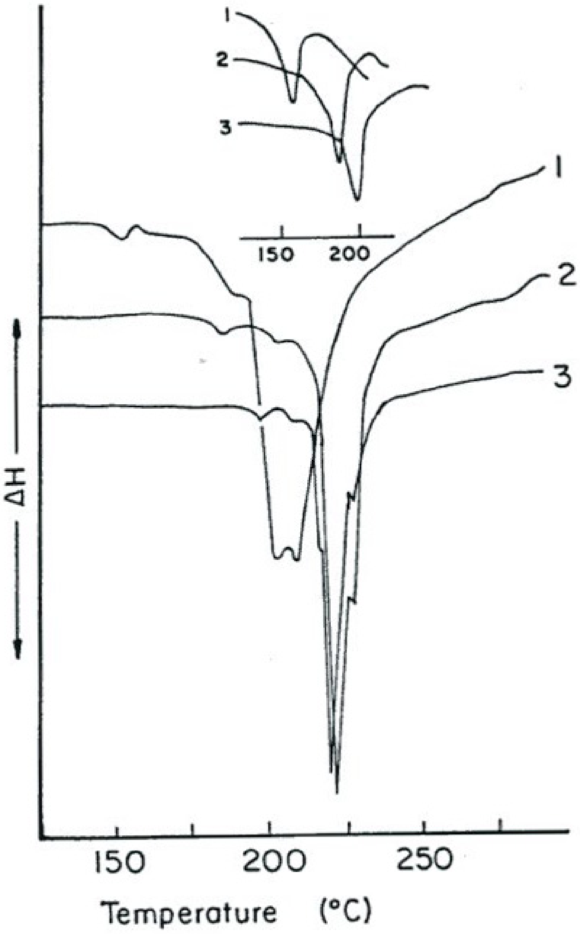


Figure 9. DSC curves of VA–MA–AA terpolymers with different compositions: AN (mg KOH/g) = 725.4 (1), 711.2 (2) and 703.4 (3). Heatig rate of 5°C/min in nitrogen atmosphere.

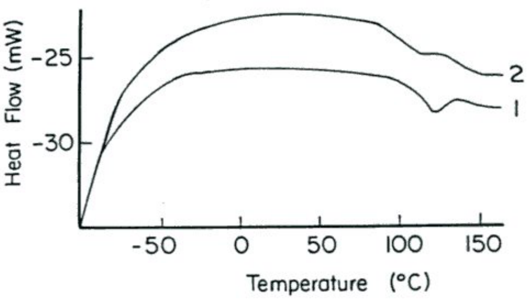


Figure 10. DSC curves of VA (33.9 mol %)–MA–AA (21.0 mol %) and VA (20.1 mol%)- –MA–MAc (57.1 mol %) terpolymers recorded beginning from −100°C. Other conditions as in Fig. 9.

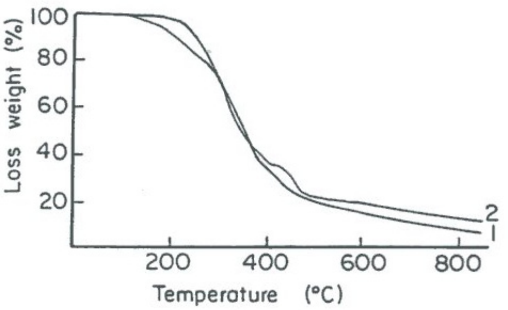
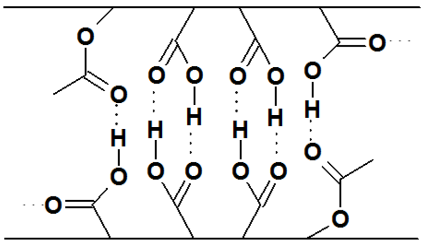


Figure 11. TGA curves of (1) VA(33.9 mol %)–MA–AA(21.0 mol %) terpolymer and (2) its hydrolized derivative. Heating rate 5°C/min in nitrogen atmosphere.

macromolecules. The average value of T_g/T_m ratio (Table 6) is approximately equal to 0.91 which is agreeable to known value of this relationship (0.93) for polar polymers proposed by Boyer.[27] The molecular organization through intermolecular H-bonding for poly(AA-*co*-MA-*co*-VA) terpolymer macromolecules, especially for its hydrolyzed derivative can be illustrated as follows:



DSC curves of poly(AA-*co*-MA-*co*-VA) and poly(VA-*co*-MA-*co*-MAc) terpolymers (Figure 10) recorded beginning -100°C show that T_g endotherm is essentially shifted to relatively low temperature region (from 186.5 to 125°C for poly(AA-*co*-MA-*co*-VA) terpolymer). This fact can be explained by change of crystallization mechanism and by formation of more strong H-compelled macromolecules with different physical structural fragments in lower temperature condition.

TGA curve of hydrolyzed terpolymer differs from same curve of initial terpolymer and has multi-step character of decomposition process (Figure 11). A first step of decomposition is related to decarboxylation reaction, i. e., transfer acid units to anhydride forms in side-chain of macromolecules.

As a result of x-ray studies, It was shown that all polymers have crystallinity except poly(MA-alt-VA) copolymer. Vinyl acetate (VA) gives the amorphous character to the polymer samples. poly(AA-*co*-MA-*co*-VA) (15.3:48.3:36.4) has also more amorphous properties than the poly(AA-*co*-MA-*co*-VA) (19.7:50.0:30.3) and poly(AA-*co*-MA-*co*-VA) (21:45.2:33.8) terpolymers. When the vinyl acetate composition increase in the terpolymers system, degree of the crystallinity decreases. Because of the chain mobility of the acetate group gives amorphous character and prevent the formation of crystalline forms. Besides effects of vinyl acetate, acrylic acid composition increment increase the crystallinity in the polymer. H-bonding effect in the polymer gives crystallinity to the polymer. As can be seen from diffraction patterns of Poly(MA-*alt*-AA) and poly(MA-*ran*-MAc) copolymers (Figure 12), these two polymers have noticeable crystallinity (40 %). So, the certain structures of these polymers may be determined by obtaining single crystal forms. It can be said that, the molecular and crystal structures of poly(MA-*alt*-AA) copolymer and poly(AA-*co*-MA-*co*-VA)(15.3:48.3:36.4), (19.7:50.0:30.3) and poly(AA-*co*-MA-*co*-VA) (21:45.2:33.8) are very similar due to common four peaks in the patterns and they have the same molecular groups. This molecular group is partially hydrolyzed anhydride group and from the maleic anhydride units [29]. And this group easily undergo H-bonding with acrylic acid units. This seems to be related to the crystalline phase, which is formed through intermolecular H-bonding between –COOH group containing functional macromolecules. Changing degree of crystallinity according to the increasing –COOH (from acrylic acid and partially hydrolyzed anhydride unit) groups are illustrated in Figure 11. Synthesized poly(MA-*alt*-AA) and poly(AA-*co*-MA-*co*-VA) terpolymer is easily dissolved in water. This solution process is accompanied by full hydrolysis of anhydride units and formation of strong H-bonding intermolecular fragments. In this case, the characteristic bands of compelled OH groups are appeared in the field

Table 6. H-Bonding effect on glass-transition (T_g), melting (T_m) and destruction (T_d and ΔH_d) behaviors of VA–MA–AA terpolymer with different compositions.

Terpolymer Composition (mol %)			AN (mg KOH/g)	T_g(C⁰)	T_m(C⁰)	T_g/T_m	T_d(C⁰)	ΔH_d(J/g)
m_1	m_2	m_2						
30.34	50.02	19.64	729.3	146.0	161.3	0.905	198	405
32.53	50.23	17.24	725.4	153. 4	182.5	0.842	207	412
33.58	45.15	20.97	711.2	186.5	201.0	0.928	218	439
35.05	45.05	19.45	703.4	197.5	206.3	0.957	219	456

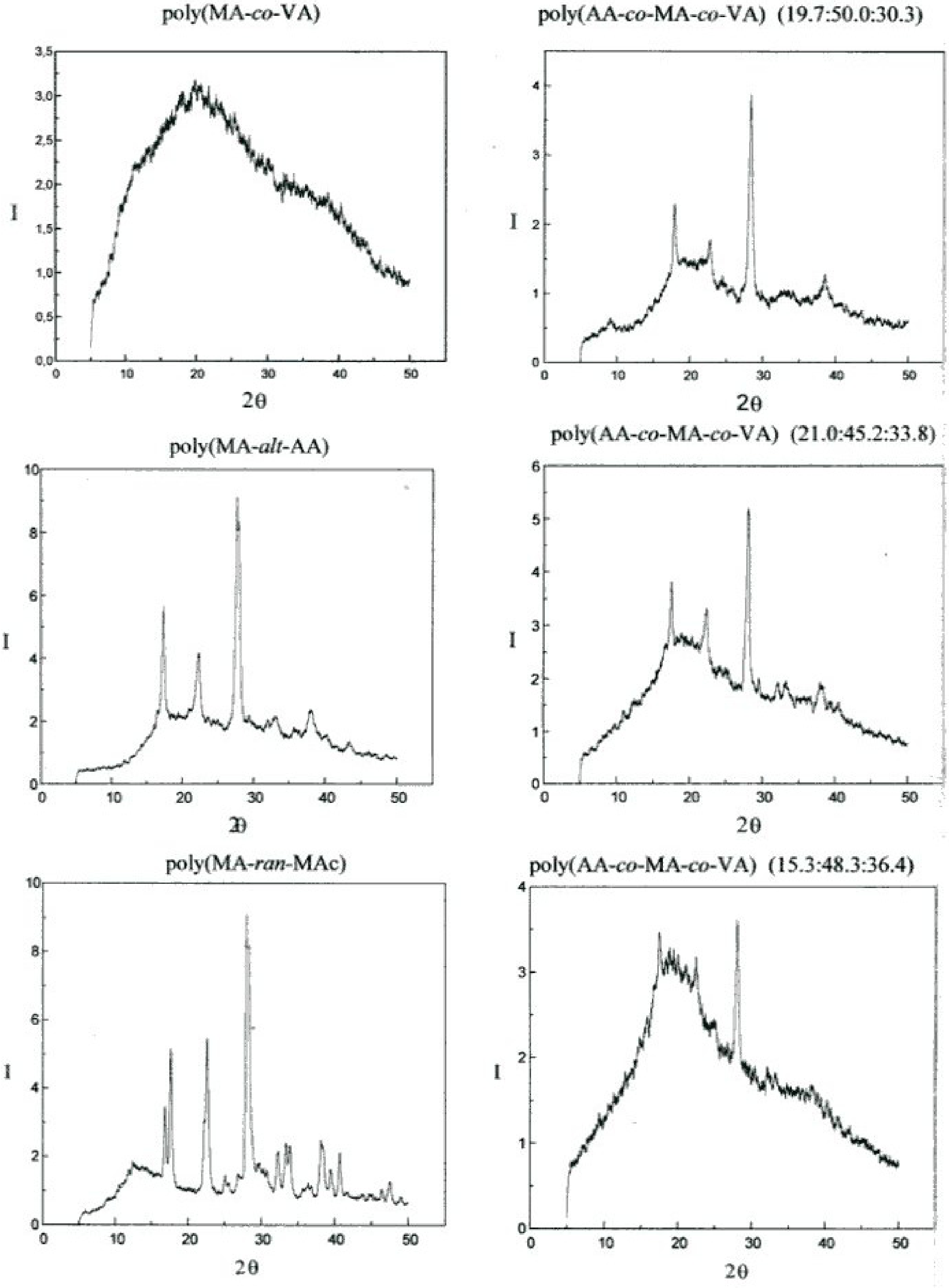


Figure 12. X-ray diffraction patterns of polymer samples.

of 2575 and 1945 cm^{-1}, intensities of which also is changed depending on –COOH content. Same opening anhydride ring also is partially proceed in the presence of atmospheric H_2O. It is clearly seen that some relationship between structure and glass-transition or melting behaviors of hydrolyzed terpolymer takes place. Hydrolyzed terpolymer again accepts an initial form by anhydridization of dicarboxylic units through thermotreatment of its thin coating or film at 120-130°C during 15 min. It is interesting that anhydridization via decarboxylation reaction does not excite crosslinking (intermolecular anhydridization) and due to regular structure of macromolecules this reaction proceeds selectively having only intramolecular character which is confirmed by its solubility and identical structure as initial poly(AA-*co*-MA-*co*-VA) terpolymer. In FTIR spectra of this terpolymer, the characteristic bands for anhydride units (1836 and 1766 cm^{-1}) are appeared, 1945 and 1630 cm^{-1} bands related to maleic acid units are disappeared and 2575 cm^{-1} is shifted to 2545 cm^{-1} field related to AA units. Similar effect is not observed for hydrolyzed poly(VA-*co*-MA-*co*-MAc) terpolymer having dominantly random monomer unit composition and partially transferred to non-soluble form after thermotreatment in analogous conditions.

REFERENCES

1. V.A. Kabanov and D.A. Topchiev, Polymerization of Ionizated Monomers, Nauka, Moscow, 1975.
2. V.A. Kabanov, V.P. Zubov and Y.D. Semchikov, Complex-Radical Polymerization, Chemistry, Moscow, 1987.
3. G.A. Jeffrey, " An Introduction to Hydrogen Bonding" Oxford University Press, New York, 1997.
4. T. Kato, N. Mizoshita and K. Kanie, Hydrogen-Bonded Liquid Crystalline Materials: Supramolecular Polymeric Assembly and the Induction of Dynamic Function, Macromol. Rapid Commun., 22 (2001) 797.
5. P. V. Shibaev, S.L. Jensen, P Andersen, K Schaumburg, V. Plaksin, Multicomponent Hydrogen-Bonded Liquid Crystalline Mixtures, Macromol. Rapid Commun., 22 (2001) 493.
6. R. Kerber, H. Hlaman, Makromol Chem., 144 (1971) 1.
7. S. Viswanathan, M.D. Dadmun, Formation of a True Molecular Composite using Optimal Hydrogen Bonding, Macromol. Rapid Commun., 22, 779 (2001).
8. M.M. Coleman, P.C. Painter, Hydrogen bonded polymer blends, Prog Polym Sci., 29 (1995) 1.
9. M. M. Coleman, Y. Xu, P.C. Painter, Compositional heterogeneities in hydrogen-bonded polymer blends: infrared spectroscopic results, Macromol., 27 (1994) 127.
10. M.M. Coleman, F.J. Graf, P.C. Painter, Specific Interactions and the Miscibility of the Polymer Blends, Technomic Publishing, Lancaster, PA, 1991.
11. M.M. Coleman, G.J. Pehlert, P.C. Painter, Functional Group Accessibility in Hydrogen Bonded Polymer Blends, Macromolecules, 29 (1996) 6820.
12. A.A. El'Saied, S.Y. Mirlina, V.A. Kargin, Copolymerization of unsaturated mono- and dibasic acids, The possibility of controlling copolymer composition Polymer Science USSR., A11 (1969) 314.
13. G.E. Ham, Reactivity of Polar monomers in Copolymerization, J. Polym. Sci., 14 (1954) 87.
14. Z.M.O. Rzaev, Topics in Current Chemistry: Organotin Compounds, Springer-Verlag, Berlin-Heidelberg-New York, 104 (1982) 107.
15. Z.M.O. Rzaev, Complex-radical alternating copolymerization, Prog. Polym. Sci., 25 (2000) 163.
16. J.M.G. Cowie, Alternating Copolymers, Plenum Press, New York, 1985.
17. S. Toppet, M. Slinckx, G. Smets, Influence of the reaction medium on the composition and the microstructure of styrene–acrylic acid copolymers, J. Polym. Sci. Polym. Chem. Ed., 13 (1975) 1879.
18. G.E. Kline, Analytical Chemistry of Polymer, Interscience Publishers, John Wiley & Son, New York-London, 1962, Vol. XII, Part. I.
19. G.E. Ham, Theory of copolymerization, Chapter 1. Copolymerization, Wiley, New York, 1964.
20. C. Caze, C. Loucheux , Mechanism of Alternating Copolymerization of Vinyl Acetate and Maleic Anhydride, J. Macromol. Sci. Chem., A9 (1975) 29.
21. H.A. Benesi, J.H. Hildebrand, A Spectrophotometric Investigation of the Interaction of Iodine with Aromatic Hydrocarbons, J. Am. Chem. Soc., 71 (1949) 2703.
22. J. A. A. Ketelaar, W. Vedder, The Infrared Spectrum of KHF2, J. Chem. Phys., 19 (1951) 654.
23. M.W. Hanna, A.L. Ashbaugh, Nuclear Magnetic resonance study of molecular complexes of 7,7,8,8, tetracyanoquinondimethane and aromatic donors, J. Phys. Chem., 68 (1964) 811.
24. T. Kelen, F. Tüdös, Analysis of the Linear Methods for Determining Copolymerization Reactivity Ratios. I. A New Improved Linear Graphic Method, J. Macromol . Sci. Chem., A9(1975) 1.
25. Z.M.O. Rzaev, Complex-radical terpolymerization of glycidyl(methyl) methacrylates, styrene and maleic anhydride, J. Polym. Sci. Polym. Chem., A37 (1999) 1095.

26. L.H. Sperling, Introduction to Physical Polymer Science, John Wiley & Sons Inc.,NewYork, (1992) 209.
27. R.F. Boyer, in Encyclopedia of Polymer Science and Technology, Suppl. Vol. 2, Interscience: New York, (1977) 745.
28. H. Kaplan Can, Z.M.O. Rzaev, A. Güner, Hydrogen (H)-complex formation of maleic anhydride acrylic acid (methyl acrylate) monomer system, J. Molec. Liq., 111 (2004) 77.
29. H. Kaplan Can, A.L. Doğan, Z.M.O. Rzaev, A.H. Uner, A. Güner, Synthesis, characterization, and antitumor activity of poly(maleic anhydride-co-vinyl acetate-co-acrylic acid) J Appl. Polym Sci, 100 (2006) 3425.