

Mechanisms of Molecular Interactions in Polybase–Polyacid Complex Formed by Copolymers of *N,N*-Dimethylaminoethylmethacrylate with Alkylmethacrylates and Methacrylic Acid with Ethylacrylate

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ABSTRACT: Mechanisms of molecular interaction in the blends of a polybase, a copolymer of *N,N*-dimethylaminoethylmethacrylate with methylmethacrylate and butylmethacrylate (PDMAEMA–MMA/BMA), with a polyacid, a copolymer of methacrylic acid with ethylacrylate (PMAA-co-EA), and plasticizer, triethylcitrate (TEC), have been investigated with FTIR Spectroscopy and potentiometry. To evaluate the strengths of hydrogen and ionic bonds in the polyelectrolyte complexes, quantum-chemical calculations were performed. According to this analysis, the energy of ionic and hydrogen bonding diminishes in the order: multi-component complexes involving protonated aminogroup of DMAEMA (ammonium cation) in the presence of chlorine counterion with ionized or unchanged carboxyl groups and water molecules (690–520 kJ/mol) > ternary H-bonded acid-base complexes associated with molecule of water (520–420 kJ/mol) > binary ionic complex of carboxylate anion and ammonium cation (404 kJ/mol) > H-bonded complex of carboxylate and ammonium ions (257 kJ/mol) > binary H-bonded complex of

uncharged carboxyl group with ammonium cation (114 kJ/mol) > ternary H-bonded complex of uncharged carboxyl group, aminogroup and water molecule (43 kJ/mol) > binary H-bonded complex between nonionized carboxyl and amino groups (26 kJ/mol). Proton-donating capability of functional groups in the studied polyelectrolyte blends diminishes in the order: $\text{HN}^+(\text{CH}_3)_2 - > \text{HOOC}- > \text{HO}-$. The proton-donating capacity can be significantly improved in the presence of Cl^- ions, the effect of which may be appreciably inhibited if Na^+ cations are available in the blend or solution. Proton-accepting capability weakens in the order: uncharged aminogroup > carboxylate anion > uncharged carboxyl group > hydroxyl group. The results of quantum chemical calculations facilitate interpretation of FTIR spectra. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1142–1165, 2009

Key words: polymer blends; polyelectrolyte complexes; hydrogen bonding; ionic bonding; complex structure and energy

INTRODUCTION

Phase state and physical properties of polymer materials are a function of their chemical structure.^{1–3} If Quantitative Structure-Property Relationship (QSPR) is known, a number of fundamental physical characteristics of polymers may be predicted from their chemical structure.^{4,5} Numerous correlations have been reported in literature between the phase state and the chemical structure of polymers^{6–8} and mo-

lecular interactions in polymer blends.⁹ In turn, on a macroscopic scale the physical properties of polymer materials are governed by their phase state and, consequently, by the molecular structure.^{10–15}

From the practical point of view, knowledge of the structure–property relationship is of considerable importance for rational design of new materials with tailored performance properties. The final goal of our research is molecular design of new pressure-sensitive adhesives (PSA) by blending of nonadhesive polymers. The PSA are viscoelastic polymer materials capable of forming strong adhesive bond with substrates of various chemical nature under application of a slight pressure (1–10 Pa) over a short period of time (1–2 s).¹⁶ On a molecular level, pressure sensitive adhesion is a result of a specific balance between high energy of intermolecular cohesion and large free volume.^{17,18} Hence, to develop

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PSA rationally we should identify the molecular structures that meet these requirements.

As recent investigations in our group have shown, mechanisms of interpolymer and polymer-oligomer complex formation can serve as underlying basis for the molecular design of new pressure-sensitive adhesives prepared by blending of nonadhesive polymers and oligomers.^{19,20} In polymer blends involving the formation of interpolymer complex between macromolecules of a polybase and a polyacid, high cohesion strength is provided by hydrogen, electrostatic, or ionic bonding between macromolecules carrying complementary groups in main chains, whereas large free volume can result from the occurrence of loops and other defects of supramolecular network structure. Within the frameworks of our molecular design method, both the energy of intermolecular cohesion of the interpolymer complex and, consequently, adhesion strength are defined by the amount and the strength of interchain crosslinking bonds. While the phase state, adhesive, mechanical and other performance properties of the PSA based on interpolymer complexes will be a subject of our subsequent publications, this article of the series focuses on the mechanisms of molecular interactions in the binary and ternary blends of polybase and polyacid with and without appropriate plasticizer.

Although a considerable amount of research work has been performed on the formation and properties of interpolymer complexes,²¹⁻²⁷ there is a lack of investigations aimed at mechanisms of molecular interaction between functional groups of complementary macromolecules in blends.²⁸⁻³⁰ Using FTIR Spectroscopy we recently studied molecular mechanisms of competitive hydrogen bonding in the triple blends of poly(*N*-vinyl pyrrolidone), PVP, with oligomeric polyethylene glycol, PEG, and a copolymer of methacrylic acid with ethyl acrylate, PMAA-*co*-EA.³¹ In the PVP-PEG-PMAA-*co*-EA blends the interpolymer complex between polybase PVP and polyacid PMAA-*co*-EA is combined with polymer-oligomer PVP-PEG complex. To evaluate the relative strengths of hydrogen bonded complexes of different molecular structure in the PVP-PEG-PMAA-*co*-EA blends, quantum-chemical calculations were performed. Obtained results allowed us to gain a molecular insight into phase state, viscoelastic behavior and adhesion of the PVP-PEG-PMAA-*co*-EA blends.³² The mechanism of molecular interaction in polymer-oligomer PVP-PEG adhesive polycomplex was earlier characterized by FTIR Spectroscopy.³³⁻³⁵ In the present study we apply this earlier developed approach to the adhesive blend of polybase, copolymer of *N,N*-dimethylaminoethyl methacrylate with methylmethacrylate and butylmethacrylate (PDMAEMA-*co*-MMA/BMA), and polyacid, copolymer of methacrylic acid with ethylacrylate (PMAA-*co*-EA), and plasticizer, triethylcitrate (TEC).

MATERIALS AND METHODS

As a polybase in this work we used the copolymer of *N,N*-dimethylaminoethyl methacrylate (DMAEMA) with methyl methacrylate (MMA) and butylmethacrylate (BMA), PDMAEMA-*co*-MMA/BMA (mole ratio 2 : 1 : 1, molecular weight 150,000 g/mol). The polybase is commercially available from Röhm Pharma GmbH, Darmstadt, Germany as Eudragit® E-100. As polyacid we employed a copolymer of methacrylic acid (MAA) with ethylacrylate (EA), PMAA-*co*-EA (mole ratio 1 : 1, molecular weight 250,000 g/mol), which was obtained as Eudragit® L-100-55 from Evonik Degussa Corp., Piscataway, NJ, USA, subsidiary of Evonik Röhm GmbH, Germany. Both polymers are amorphous.

Preparation of polyelectrolytes charged to a predetermined degree of dissociation of ionogenic groups was provided by the treatment of their water-alcohol (50 : 50) solutions by aqueous solutions of HCl (for polybase) or NaOH (for polyacid). With this purpose the amounts of HCl or NaOH required for full ionization of the ionogenic groups was measured in advance with potentiometric titration. The degrees of polyelectrolyte ionization of 10 and 50% corresponded, respectively, to 0.1 and 0.5 of the gram equivalents of the HCl and NaOH required for full ionization of the polyelectrolyte.

Plasticizer, employed in this work, was triethyl citrate, TEC, obtained from Morflex, Greensboro, NC. As low molecular weight analogues of the structure of monomeric units of polyelectrolyte backbones, the *N,N*-dimethylpropyl amine (DMPA) and isobutyric acid (IBA) were used and these were obtained from Sigma-Aldrich (Hamburg, Germany). Molecular structures of materials, employed in our research, are shown in Figure 1. All the components of binary

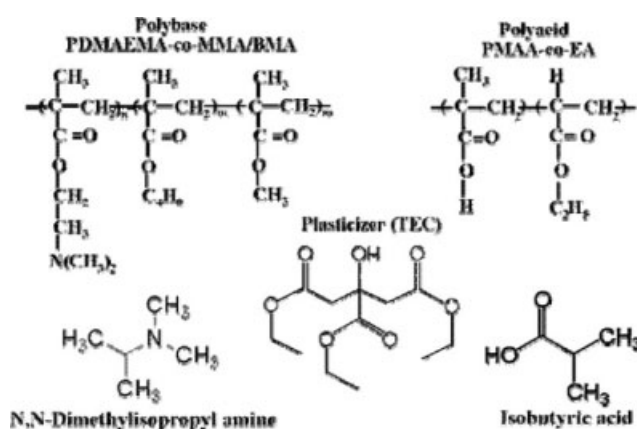


Figure 1 Molecular structures of PDMAEMA-*co*-MMA/BMA polybase ($n = 2m$), PMAA-*co*-EA polyacid, TEC plasticizer and low-molecular weight analogues of the monomeric units of polyelectrolyte backbones, DMPA and IBA.

TABLE I
Compositions of Investigated Polymer Samples

Formulation	Composition, % mass			
	Polybase, PDMAEMA-co-MMA/BMA	Polyacid, PMAA-co-EA	Plasticizer, TEC	Polyelectrolyte ionization degree
1	100	–	–	–
2	–	100	–	–
3	100	–	–	Polybase, 50%
4	100	–	–	Polybase, 100%
5	–	100	–	Polyacid, 100%
6	83.3	16.7	–	–
7	66.7	33.3	–	–
8	50	50	–	–
9	33.3	66.7	–	–
10	16.7	83.3	–	–
11	91	9	–	–
12	95.2	4.8	–	–
13	68.2	6.8	25	–
14	63.6	6.4	30	–
15	50	5	45	–
16	52.4	2.6	45	–
17	55	–	45	–
18	–	55	45	–
19	45.8	9.2	45	–
20	36.7	18.3	45	–
21	25.2	25.5	45	–
22	18.3	36.7	45	–
23	9.2	45.8	45	–
24	5	50	45	–
25	2.6	52.4	45	–
26	87.5	12.5	–	Polybase, 100%
27	91	9	–	Polybase, 100%
28	91	9	–	Polyacid, 100%
29	91	9	–	Polybase, 10% and Polyacid, 10%
30	1	0.335	–	Polybase, 100%
31	83.3	16.7	–	Polybase, 100%
32	66.7	33.3	–	Polybase, 100%
33	50	50	–	Polybase, 100%
34	33.3	66.7	–	Polybase, 100%
35	16.7	83.3	–	Polybase, 100%
36	59.1	5.9	35	–

and ternary polybase–polyacid–plasticizer blends as well as DMPA and IBA were used as received.

The polybase–polyacid blends with and without plasticizer were prepared by casting–drying method from ethanol solutions. Required amount of polybase was first dissolved in ethanol under vigorous stirring (600–700 rpm) using a Cole-Parmer (USA) laboratory mixer (model 50002-25). Stirring rate was then increased to 900–1000 rpm and the PMAA-co-EA polyacid was slowly added. This solution was then kept stirred for 16 h until homogeneous solution was obtained. TEC plasticizer was added to the polymer solution under stirring with magnetic stirrer. The total concentration of polymers in ethanol averaged 38–40 wt %. The homogeneous solution was cast onto a polyethylene terephthalate (PET) casting sheet PEBA-X-600. A uniform thickness of the films was obtained by using the BYK-Gardner film casting knife (AG-4300 Series) as described earlier.³⁶

The wet film thickness was 0.5 mm and the thickness of dry film was 80–100 μm . The films were dried overnight at ambient conditions (19–22°C). Upon drying, the films were covered by the second sheet of the PEBA-X-600 release liner. The compositions of prepared polyelectrolyte blends are listed in Table I.

Potentiometric titration was performed with Ecotest-120 pH-meter, obtained from Econix, Moscow, Russia. During polyacid titration, the 0.2N water-alcohol solution of PMAAA-co-EA was employed as an analyte and 0.05N polybase solution was used as a titrant, whereas the pH of their mixtures was monitored with a calibrated pH-sensitive glass electrode. For determination of gram equivalents of the HCl and NaOH needed for complete ionization of polyelectrolytes, the polyelectrolyte analyte was first dissolved in 1 : 1 mixture of ethyl alcohol with distilled water and obtained 1% solution was then

titrated by 0.2N HCl or 0.1N NaOH aqueous solutions. Titration curves had a characteristic sigmoid shape. The section of the curve that demonstrates the maximum pH change marks the equivalence point of the titration.

FTIR spectra of the blends and parent components within the range of wavenumbers 4000–400 cm^{-1} were recorded using Bruker IFS-113v and IFS-66 v/s spectrometers (Germany) with a resolution of 1 cm^{-1} . Four hundreds scans were performed for each spectrum. Films used as specimens were cast on Si plates from 15 to 20% ethanol solutions followed by drying for 24 h at ambient temperature. The thickness of dry films was 10–15 μm . The spectra were treated using GRAMS program (Microsoft) and OPUS (Bruker). Quantum chemical calculations were performed with complete optimization of geometric parameters by means of minimization of energy within the frameworks of Chem Office 2004 using MOPAK software. Evaluation of charges at the atoms and interaction energy was performed with GAUSSIAN semiempirical approach in DFT approximation.³⁷

RESULTS AND DISCUSSION

Identification of interacting functional groups in polybase–polyacid–plasticizer blends with FTIR Spectroscopy

FTIR Spectra of Unblended Polyelectrolytes and Plasticizer

FTIR spectrum of PDMAEMA-*co*-MMA/BMA polybase (Formulation 1, Table I) is presented in Figure 2. All the bands of this spectrum are easily identified with the functional groups of the copolymer as indicated in the Figure 2.^{38,39} The bands of N-C bond of low intensity in the area of 1100–1200 cm^{-1} are obscured by the stretching and bending vibrations of

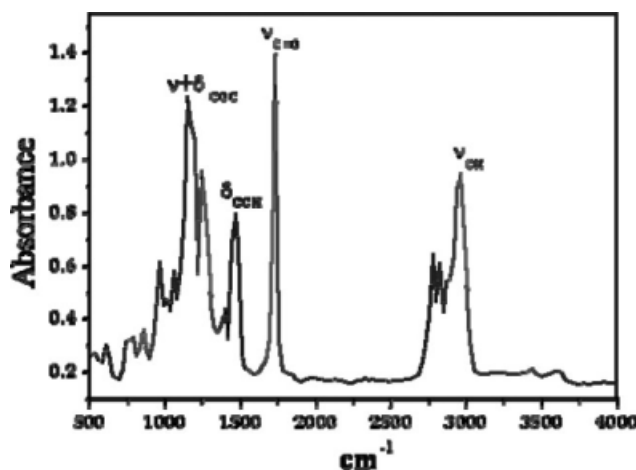


Figure 2 FTIR spectrum of uncharged PDMAEMA-*co*-MMA/BMA polybase (Formulation 1).

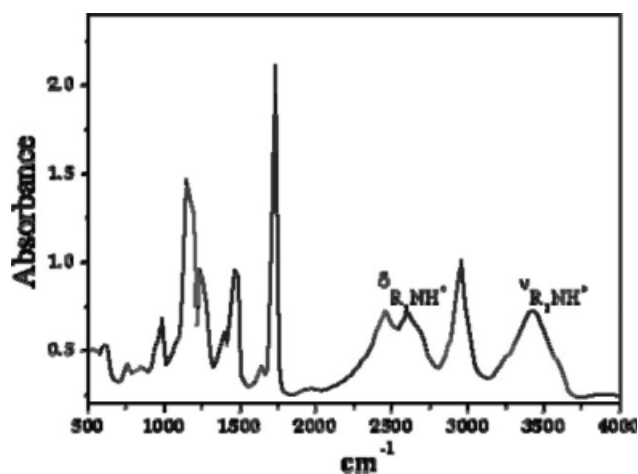


Figure 3 FTIR spectrum of PDMAEMA-*co*-MMA/BMA polycation, protonation degree is 100% (Formulation 4).

C—O—C ester groups in alkylacrylate MMA/BMA units. Two bands at 2776 and 2821 cm^{-1} relate to the stretching vibrations of two neighboring methyl groups at the nitrogen atom.

Figure 3 demonstrates FTIR spectrum of completely protonated PDMAEMA-*co*-MMA/BMA copolymer (Formulation 4, Table I). Within the range between 500 and 1200 cm^{-1} the changes are insignificant, but two new broad bands in the area of $\delta = 2250\text{--}2750$ cm^{-1} and $\nu = 3200\text{--}3470$ cm^{-1} refer, correspondingly, to bending, δ , and stretching, ν , vibrations of ammonium $\text{—NH}(\text{CH}_3)_2^+$ cation. The complicated profile of these bands can be explained by association of a proton of the ammonium cation with water molecules and different mechanisms of both intra and intermacromolecular association of cationic groups.

In the PMAA-*co*-EA spectrum (Formulation 2, Fig. 4) there exist two bands relating to carboxyl groups: at 1710 cm^{-1} (monomeric form) and 1698 cm^{-1}

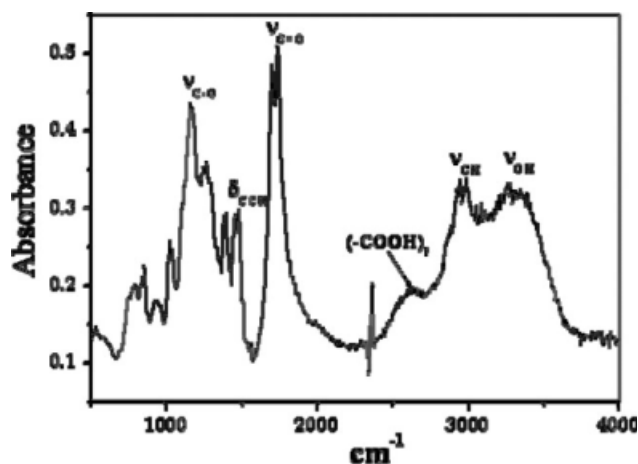


Figure 4 FTIR spectrum of PMAA-*co*-EA polyacid (Formulation 2).

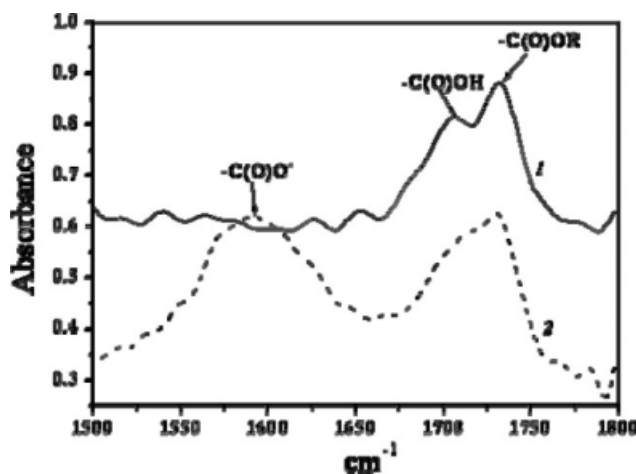


Figure 5 Comparison of FTIR spectra of uncharged PMAA-co-EA polyacid (1, Formulation 2) and PMAA-co-EA polyanion of 50% degree of carboxyl group dissociation (2, Formulation 3).

(associated form).^{31,39} Referring the band at 1700 cm^{-1} to carboxyl group of MAA monomer unit doesn't mean that the group is free from association. It can be associated with other carboxyl group but without formation of cyclic dimer. The broad band at 2600 cm^{-1} in the PMAA-co-EA spectrum confirms the presence of eight-membered cyclic dimers of carboxyl groups.³¹

Figure 5 compares FTIR spectrum of uncharged PMAA-co-EA polyacid and the spectrum of corresponding polyanion with 50% degree of neutralization of carboxyl groups (Formulation 3, Table I). A broad band of high intensity between 1700 and 1720 cm^{-1} characterizes nonionized carboxyl groups, whereas the band at 1575 cm^{-1} relates to the carboxylate ions. The band 1700 – 1715 cm^{-1} , featured for uncharged carboxyl groups, is seen in the spectrum of polyacid with 50% content of anionic groups as a shoulder of carbonyl group stretching vibrations ($\nu_{\text{C=O}}$).

In this way, the data of FTIR spectroscopy make feasible identification of charged and nonionized functional groups in polybase and polyacid macromolecules. At the same time, the breadth and complex profile of spectrum bands indicates that in unblended polymers different functional groups are involved into various mechanisms of interaction with the groups of the same or neighboring macromolecule, which are similar on bonding energy.

Figure 6 illustrates FTIR spectrum of TEC plasticizer. The presence of hydroxyl groups in TEC molecules (see Fig. 1) causes a broad asymmetric band at 3497 cm^{-1} . The most intensive peaks at 1730 cm^{-1} ($\nu_{\text{C=O}}$) and 1000 – 1200 cm^{-1} ($\nu, \delta_{\text{C-O-C}}$) relate to the ester-C(O)OR groups.

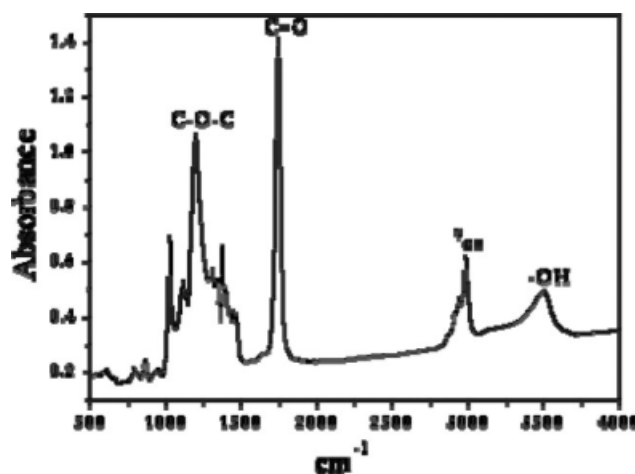


Figure 6 FTIR spectrum of TEC plasticizer.

FTIR Spectra of Binary Polybase–Polyacid Blends

The data of FTIR Spectroscopy provide unambiguous identification of interacting functional groups in complementary macromolecules of polybase and polyacid. The formation of hydrogen and ionic bonds between functional groups is manifested in the IR spectra by the shift of their characteristic frequencies toward lower wavenumbers.

Mixing of uncharged polybase and polyacid macromolecules results only in hydrogen bonding between their amino and carboxyl groups as is evidenced by the lack of bands featured for ammonium (2250 – 2750 cm^{-1}) and carboxylate (1530 – 1590 cm^{-1}) ions (Fig. 7). This H-bonded complex formation between uncharged polybase and polyacid macromolecules proceeds following the mechanism of neutralization reaction (1):

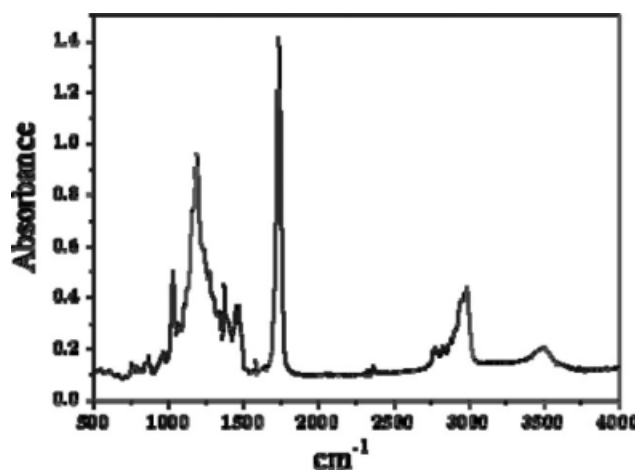


Figure 7 FTIR spectrum of uncharged polybase–polyacid 10 : 1 mixture, Formulation 11, Table I.

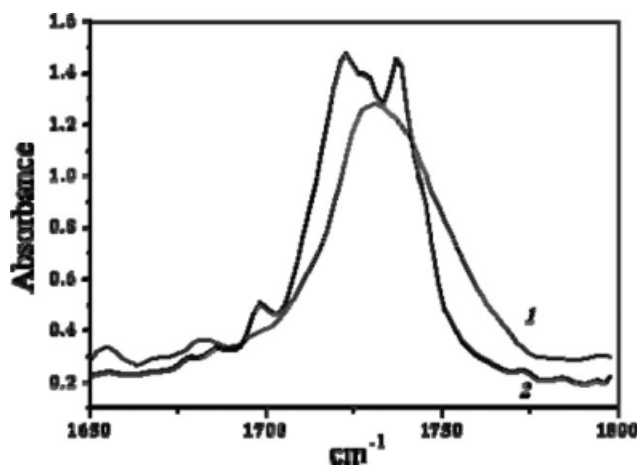
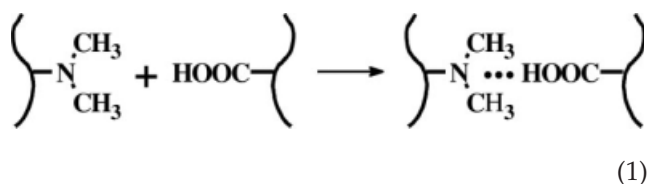


Figure 8 Comparison of FTIR spectra of uncharged PDMAEMA-*co*-MMA/BMA polybase (1, Formulation 1) and its mixture with uncharged PMAA-*co*-EA polyacid (10 : 1, Formulation 11, curve 2) in the range of carbonyl group stretching vibrations.



However, compared with FTIR spectra presented in Figures 8 and 9, the state of carbonyl groups changes appreciably under polybase mixing with polyacid. A single broad band of C=O bonds at 1730 cm^{-1} in polybase spectrum splits into few bands as 10% of polyacid is added (Formulation 11, Fig. 8). Similar effect is observed for any polybase: polyacid ratios, the increase of polyacid content in the blends affects only the relative intensities of separate bands.

FTIR Spectra of Polyelectrolyte Blends Involving Ionized Functional Groups

FTIR spectra in Figure 10 are informative on the interaction of PDMAEMA-*co*-MMA/BMA polycation with macromolecules of uncharged PMAA-*co*-EA polyacid. A complex profile of the wide band between 2350 and 2750 cm^{-1} in polycation spectrum (Fig. 10, curve 1) indicates an occurrence of different dimer and monomeric forms of ammonium cation, which, in turn, may be associated with water molecules. Appreciable width of this band is supposed to signify close values of formation energies of these complexes. Mixing the polycation with polyacid results at first in the decrease of intensity of this wide band (Fig. 10, curve 2, Formulation 31 in Table I) and then its vanishing in the blends containing an excess of uncharged polyacid macromolecules (Curve 3, Formulation 35). Instead a new wide band

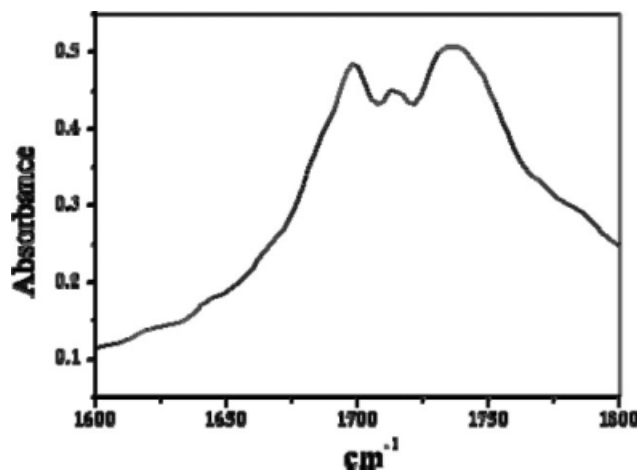


Figure 9 FTIR spectrum of PMAA-*co*-EA polyacid (Formulation 2) in the range of carbonyl group stretching vibrations.

of 2600 – 3200 cm^{-1} arises, implying that the product of polycation interaction with uncharged polyacid has a particular structure.

The data of potentiometric titration shown in Figure 11 allow us to gain a further insight into the nature of uncharged polyacid interaction with PDMAEMA-*co*-MMA/BMA polycation in water-alcohol solutions. Although both analyte and titrant solutions have identical pH values, the pH of their mixture is appreciably lower implying the occurrence of exchange reaction (2):

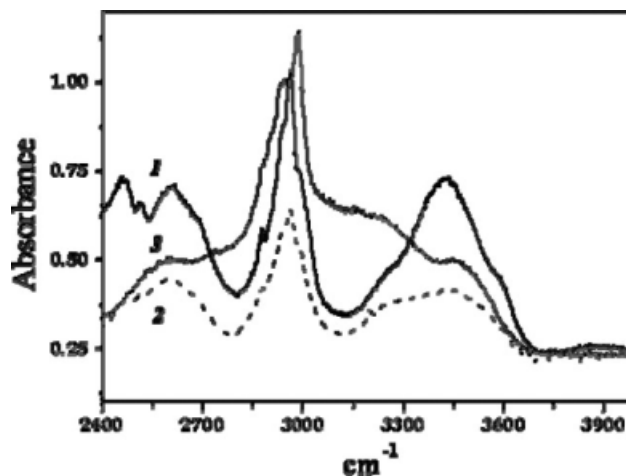
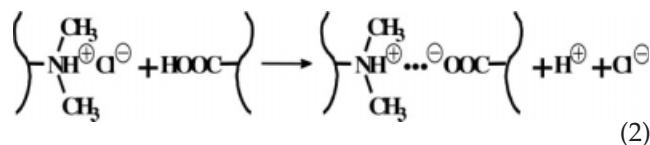


Figure 10 Comparison of FTIR spectra of PDMAEMA-*co*-MMA/BMA polycation (1, Formulation 4) and its blends with uncharged macromolecules of PMAA-*co*-EA polyacid in the component ratios of 5 : 1 (2, Formulation 31) and 1 : 5 (3, Formulation 35) within the range of N–H bond stretching vibrations.

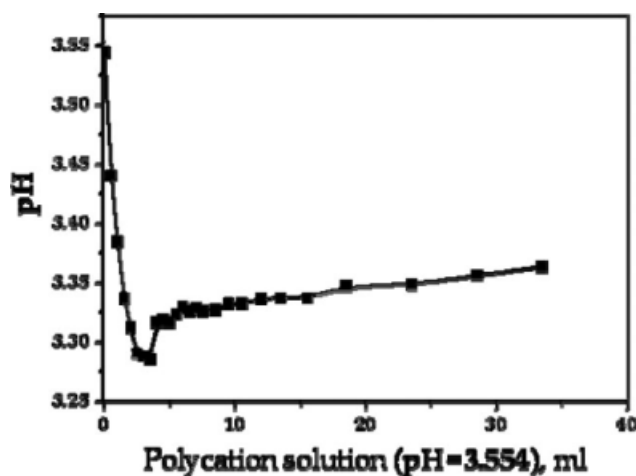


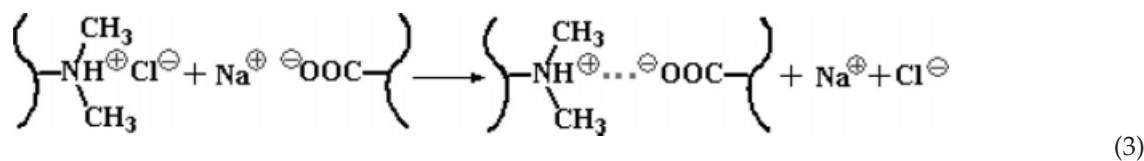
Figure 11 Potentiometric titration curve of 0.2N PMAA-*co*-EA polyacid solution (analyte) by 0.05N solution of PDMAEMA-*co*-MMA/BMA polycation (titrant). pH values of both analyte and titrant solutions are identical (pH = 3.55).

As a result of this reaction, a strong inorganic acid (HCl) is driven out of the salt by a weak organic polyacid. In the literature on the formation of interpolyelectrolyte complexes in solutions such exchange reactions are well documented.^{25,40} According to reaction (2), the amount of free protons formed under mixing the polyacid with polycation corresponds to the amount of ionic bonds between ammonium and carboxylate groups. In this way, the data of potentiometric titration make possible quantitative determination of binding degree in such systems.

FTIR spectroscopy data confirm ionic type of the bonds between ammonium cations in PDMAEMA-*co*-MMA/BMA side chains and PMAA-*co*-EA carboxyl groups. With this purpose we should consider the state of carboxyl groups in the polycation-polyacid

blends and analyze FTIR spectra in the area of carboxyl group stretching vibrations. Effect of protonation of polybase aminogroups on the state of carboxylic group of polyacid in the blends is illustrated in Figure 12. As polyacid is mixed with uncharged polybase (Curve 1, Fig. 12), the type of polybase-polyacid interaction is hydrogen bonding and the presence of nonionized carboxyl groups in the blends is evidenced by a $\nu_{\text{C=O}}$ shoulder at 1700 cm^{-1} on the steep slope of very intensive peak of the carbonyl groups in ester groups of copolymers. Incorporation of comparatively small amounts of PDMAEMA-*co*-MMA/BMA polycation into the blends with polyacid leads to the appearance of a series of bands in the area of longer wavelengths ($1680\text{--}1600\text{ cm}^{-1}$) relating to H-bonded associates of the ammonium cation with uncharged carboxyl groups (Curve 2, Fig. 12). The weak bands at 1575 and 1560 cm^{-1} ascertain the appearance of carboxylate anions in this blend.³⁹ As polycation concentration in the blends with polyacid increases further (Curve 3, Fig. 12), the bands of carboxyl anions at 1575 and 1560 cm^{-1} become well pronounced, whereas the bands of unionized carboxyl group (1700 cm^{-1}) vanish.

Thus the interaction between ammonium polycation and macromolecules of uncharged polyacid is so strong that ionization of carboxyl group occurs. The spectrum of the blends of PDMAEMA-*co*-MMA/BMA polycation and PMAA-*co*-EA polyanion features coupling of the bands of ammonium polycation ($2250\text{--}2750$, $3200\text{--}3470\text{ cm}^{-1}$) and carboxyl polyanion (1575 , 1560 cm^{-1}). Interaction between cationic and anionic groups is accompanied with a shift of ammonium group stretching vibration toward longer wavelengths. This type of polycation-polyanion interaction can be described by the reaction of charge neutralization (3):



According to this reaction, one uncharged particle of polyelectrolyte acid-base complex is formed from two oppositely charged macromolecules. Neutralization of electrical charge generally results in the loss of solubility of the polycation-polyanion complex, which is often insoluble, and the loss of entropy of macromolecular mixing. The loss in entropy of polymer chains in the course of reaction (3) is compensated mainly by the release of low molecular mass counterions and by a higher disordering of the solvent molecules (hydrophobic interactions), meaning

that a net increase in entropy is the driving force of the process.²⁴ The long-range character of Coulomb electrostatic interactions as compared with hydrogen bonding provides the formation of the complexes with nonuniform chemical composition, stereoregularity and morphology. In such complexes of oppositely charged macromolecules, mainly, random charge-compensation is found, and in most cases the structure can be hardly improved once the complex has been formed.⁴¹

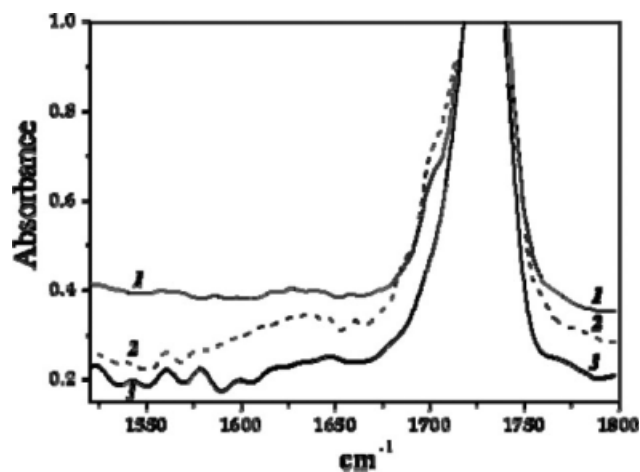


Figure 12 FTIR spectra of uncharged polybase-polyacid blend (1 : 1, Formulation 8, Curve 1), and the blends of PDMAEMA-*co*-MMA/BMA polycation with uncharged PMAA-*co*-EA polyacid in the ratios of 5 : 1 (Formulation 35, Curve 2) and 1 : 5 (Formulation 31, curve 3) in the area of carboxyl group stretching vibrations.

FTIR Spectra of Ternary Polyelectrolyte Blends with TEC Plasticizer

Up to this point we considered only binary blends of polybase with polyacid. The binary blends are not tacky and cannot be employed as pressure sensitive adhesives. Adhesive formulations based on interpolyelectrolyte complexes should additionally contain a plasticizer such as TEC. In this section we focus on the effect of TEC plasticizer on polybase-polyacid interaction.

Every TEC molecule contains only single hydroxyl group (Fig. 1) that can interact with amino and carboxyl groups in polybase-polyacid blends. The IR bands of carbonyl groups of TEC molecule are hardly discernible on the background of ester carbonyls in copolymer repeat units. As it seen from comparison of FTIR spectra presented in Figures 13 and 6, in the range of OH group vibrations the spectrum of ternary blend exhibits three comparatively slightly pronounced bands at 3619, 3498, and 3437 cm^{-1} , whereas in TEC spectrum the hydroxyl group is characterized with a single wide asymmetric band at 3497 cm^{-1} . From this fact a logical conclusion can be drawn that the middle band at 3498 cm^{-1} relates to stretching vibrations of hydroxyl groups, which are not involved into interaction with polyelectrolytes. Two extreme bands correspond, respectively, to other states of the OH groups in the ternary blends, which are strongly associated with complementary groups in the blends (3437 cm^{-1}) and less associated in unblended TEC (3619 cm^{-1}).

Ester groups are main structural elements of both TEC and copolymer macromolecules. For this reason it is of no surprise that FTIR spectra of TEC and studied polyelectrolytes are qualitatively similar in

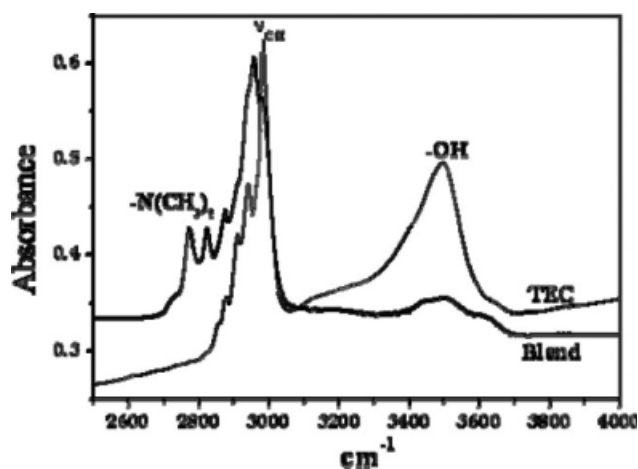


Figure 13 Comparison of FTIR spectra of ternary polybase-polyacid-TEC blend (Formulation 36, Table I) and unblended TEC in the range of hydroxyl group stretching vibrations.

the area of ester group vibrations (Figs. 2, 4, 6). Indeed, most intensive bands at 1730 cm^{-1} ($\nu_{\text{C=O}}$) and 1000–1200 cm^{-1} ($\nu_{\text{C-O-C}}$ and $\delta_{\text{C-O-C}}$) are observed in both spectra. Nevertheless, in the blend spectrum these bands are shifted more than by 10 cm^{-1} toward longer wavelengths, indicating stronger association of ester groups in ternary polybase-polyacid-TEC blends as compared with unblended TEC.

As for ternary TEC blends with ionized polyelectrolytes, the effect of TEC on interaction of polycation with uncharged or ionized polyacid is negligible in comparison with much stronger effect of charged macromolecules.

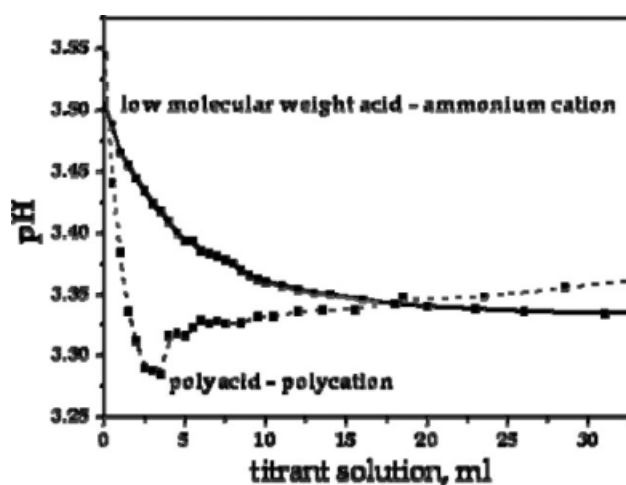
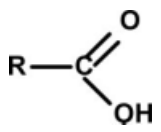
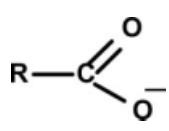
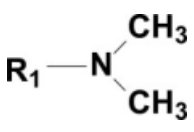
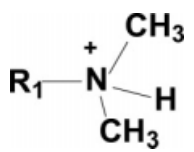


Figure 14 The curve of potentiometric titration of low-molecular weight analogue of polyacid monomer unit (IBA, pH = 3.415) by the analogue of polycation monomer unit (DMPA, pH = 3.554) in comparison with the titration curve of PMAA-*co*-EA polyacid solution (analyte) by the solution of PDMAEMA-*co*-MMA/BMA polycation (titrant) from the Figure 11. The concentrations of analyte and titrant solutions are 0.2 and 0.05N, respectively.

TABLE II
Structure and Energetic Characteristics of the Models of Polymer Functional Groups

Model	Structure	Total energy minimum, E_t (eV)	Ionization Energy (eV)	
			Calculated	Experimental ⁴²
Polyacid Carboxyl Group (1)		-1419.85131	12.81	10.7
Polyacid Carboxylate Anion (2)		-1407.04121		
Polybase Aminogroup (3)		-2418.48946	7.08	9.2 (Protonation)
Polybase Ammonium Cation (4)		-2425.57227		

$R = -C(CH_3)_3$, $R_1 = -(CH_2)_2OC(O)C(CH_3)_3$

For quantitative insight into the mechanisms of molecular interaction between functional groups of polybase and polyacid macromolecules and polycation–polyanion complexation we have performed quantum chemical calculations of the energy of complex formation for more than 230 structures.

2. Quantum chemical evaluation of hydrogen and ionic bonding in polybase–polyacid blends

Evaluation of Structural, Electronic and Energetic Characteristics of the Models of Unblended Components and their Ionized Forms

In this research we employed the models listed in Table II that have approximated functional groups of studied polyelectrolytes. In these models $R = -C(CH_3)_3$ and $R_1 = -(CH_2)_2OC(O)C(CH_3)_3$. As follows from the data in Table II, ionization energy of carboxylic group and proton affinity of aminogroup are in reasonable agreement with experimental values obtained for acetic acid and trimethylamine, respectively.⁴²

The values of bond lengths, valence angles and atom charges are presented in Table III. As these data have shown, ionization of carboxyl group is

accompanied with equalization of the length of C–O and C=O bonds and the charges at oxygen atoms, while O=C–O valence angle increases more than by 10°. Polarization of C–O and C=O bonds in anion is much greater than in carboxyl group of acid, i.e., delocalization of electron density at O=C–O group of carboxylate anion occurs.

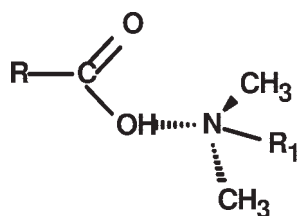
Protonation of nitrogen atom in model 3 leads to the lengthening of neighboring C–N bonds and the formation of new short N–H bond (1.03 Å). Valence C–N–C angles decrease as compared with those in uncharged aminogroup and configuration of trigonal pyramid at nitrogen atom in model 3 transforms into tetrahedral configuration in model 4. Charge distribution in ammonium cation shows strong polarization of N–H bond, whereas nitrogen atom has a small negative charge.

Interaction between Uncharged Functional Groups of Polybase and Polyacid

Interaction of carboxyl group (model 1) and aminogroup (model 3) results in formation of hydrogen bonded complex (model 5):

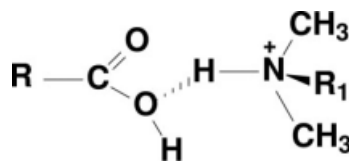
TABLE III
Major Geometric and Structural Characteristics of
Employed Models (1-4)

Characteristics	Model			
	1	2	3	4
Bond Length (Å)				
C=O	1.230	1.263	-	-
C-O	1.368	1.264	-	-
O-H	0.967	-	-	-
N-CH ₃	-	-	1.447	1.487
N-CH ₂ -	-	-	1.457	1.503
N-H	-	-	-	1.030
Valence Angle (degree)				
O=C-O	113.22	123.93	-	-
H-O-C	109.97	-	-	-
CH ₃ -N-CH ₃	-	-	112.82	110.60
CH ₃ -N-H	-	-	-	108.37
Charge (e)				
O=	-0.2979	-0.5773	-	-
-C=	+0.2970	+0.3396	-	-
-O-	-0.2904	-0.5828	-	-
H-O	+0.2231	-	-	-
N	-	-	-0.263	-0.0008
CH ₃ -N	-	-	-0.120	-0.195
-CH ₂ -N	-	-	-0.060	-0.136
H-N	-	-	-	+0.254



Model 5 (H-bonded Acid-Base complex)

The length of this H-bond is 2.545 Å and complexation energy is 26.20 kJ/mol. Interaction of carboxyl proton with nitrogen atom of aminogroup does not lead to the change of pyramidal environment of the nitrogen atom. Local geometry around the nitrogen atom is not tetrahedral, but represents distorted tetragonal pyramid with nitrogen atom in apex. The bond lengths and atom charges of hydrogen bonded and ionic acid-base complexes are listed in Table IV.



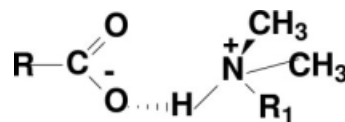
Model 6 (Acid-Ammonium Cation)

Hydrogen-bonded complex of uncharged carboxyl group with ammonium cation (model 6) exhibits much lower energetic minimum (114.00 kJ/mol, Table IV). The length of hydrogen bond is 2.408 Å, which is much shorter than in acid-base complex outlined by model 5. Tetrahedral configuration

around nitrogen atom is much more distorted in this case as compared with model 4 (ammonium cation free of hydrogen bonding), because the angles are more asymmetric.

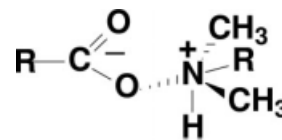
As calculations have shown, carboxyl anions are not capable of forming the complexes with uncharged aminogroups.

Hydrogen bonding can be also realized in the complex of carboxyl anion and ammonium cation (model 7).



Model 7 (H-bonded complex of carboxylate and ammonium ions)

The energy of this complex formation is 257.5 kJ/mol, and the length of hydrogen bond is 2,21 Å. Environment of nitrogen atom has tetrahedral configuration, whereas C-O and N-C bonds are strongly polarized (Table IV).

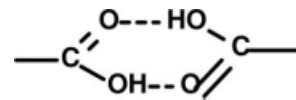


Model 8 (Ionic complex of carboxylate and ammonium counterions)

Most energetically favorable (404.36 kJ/mol) is ionic complex (model 8). A distance between oxygen atom of carboxylate anion and nitrogen atom of ammonium cation is found to be 3.41 Å. This value is in fairly reasonable agreement with the sum of ionic radii of COO⁻ anion (1.58 Å) and NH₄⁺ cation (1.43 Å).⁴³

Self-Association of Uncharged and Partially Ionized Functional Groups

Self-association of PMAA-co-EA carboxyl groups is considered in our earlier publication.³¹ As has been shown, among a variety of possible interaction mechanisms, the more energetically favorable are cyclic complexes (model 9):



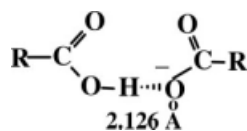
Model 9 (Self-associates of carboxyl groups)

That is characterized with the energy of complex formation of 26.477 kJ/mol. Particular features of this complex formation are described earlier³¹ and FTIR spectrum of the complex in the range of carbonyl group vibration is presented in Figure 9.

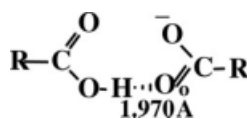
TABLE IV
Major Energetic, Geometric and Structural Parameters of Interaction Products Between Uncharged and Charged Carboxyl and Aminogroups

Characteristics	Model			
	5	6	7	8
ΔE (kJ/mol)	26.195	114.00	257.50	404.363
Bond length (Å)	2.545	2.408	2.210	3.410
—C=O	1.235	1.238	1.236	1.274
—C—O—	1.362	1.370	1.361	1.273
—O—H	0.975	0.969	2.210	—
N—CH ₃	1.447	1.485	1.447	1.486
N—CH ₂ —	1.457	1.499	1.457	1.498
N—H	2.545	1.046	0.87	1.025
Valence Angle (degree)				
O=C—O	116.66	110.98	114.55	118.97
H—O—C	109.82	110.48	130.87	—
CH ₃ —N—CH ₃	116.66	109.97	113.06	110.32
CH ₃ —N—H	109.82	107.88	109.50	108.75
Charge (e)				
O=	-0.3961	-0.3754	-0.355	-0.6161
—C=	+0.3504	+0.3333	+0.310	+0.338
—O—	-0.3861	-0.3386	-0.268	-0.6180
H—O	+0.3030	+0.2546	—	—
N	-0.3514	+0.0011	+0.091	+0.0337
CH ₃ —N	-0.2352	-0.1820	-0.200	-0.1810
—CH ₂ —N	-0.1471	-0.1190	-0.140	-0.2140
H—N	—	+0.2984	+0.252	+0.1938

In partially ionized macromolecules of polyacid, uncharged carboxyl group (model 1) can form also the complex with carboxyl anion (model 2), giving two types of the complexes outlined by models 10 and 11:



Model 10 (Carboxyl group complexes with carboxylate anion)

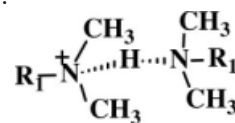


Model 11

A gain in energy under such complex formation (89.910 kJ/mol for model 10 and 73.507 kJ/mol for model 11) is appreciably greater, and the length of

bond is shorter than corresponding values for the complex described by model 9.

Two and more aminogroups (model 3) are not disposed towards self-association. However, uncharged aminogroup can form a stable complex with its own cation (model 4):



Model 12 (Associates of uncharged aminogroup with ammonium cation)

The energy of such complex formation is found to be 46.765 kJ/mol.

Equilibriums between Different Mechanisms of Molecular Interaction in Polybase–Polyacid Blends

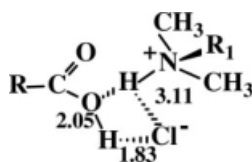
Comparison of the data listed in Table IV and calculated values of complexation energies for the models 9–12 provides an insight into possible mechanisms of molecular interactions between functional groups of

polybase and polyacid in blends. If all the functional groups are uncharged, the equilibrium will exist between self-associates of carboxyl groups (model 9) and H-bonded complexes of the carboxyl and amino groups (model 5) because the complexation energies of the models 9 and 5 are close in their values. This equilibrium is illustrated by FTIR spectra in Figures 7–9. If a part of carboxyl groups in the polyacid blends with polybase is charged, the equilibrium will be shifted to the formation of the complexes between uncharged carboxyl groups and carboxylate anions (models 10 and 11), whereas the self-associates of the carboxyl groups (model 9) and H-bonded acid-base complexes (model 5), which are appreciably less energetically favorable, will be destroyed. As the aminogroups are partially protonated by addition of a strong inorganic acid (e.g., HCl) into the blend, the equilibrium will be shifted to the complexes of uncharged carboxyl groups and ammonium cation (model 6, $\Delta E = 114.0$ kJ/mol), whereas comparatively less stable complexes of uncharged aminogroups with their cations (model 12, $\Delta E = 46.765$ kJ/mol) will hardly exist.

Lastly, if cations (model 4) and anions (model 2) are simultaneously present in the blends, the equilibrium will be shifted to the formation of much more stable ionic pairs (models 7) and ionic complexes (model 8) with a prevalence of strongest complex described by model 8.

Effect of Chlorine Counterion on Complexation of Ammonium Cation with Uncharged Carboxyl Group

Treatment of polybase–polyacid blend with HCl leads to incorporation of chlorine counterion. Introduction of chlorine counterion into the complex of carboxyl group with ammonium cation (model 6) results in the formation of the structure (model 13) in which the Cl^- anion is placed between the proton of carboxyl group and the proton of ammonium cation:



Model 13 (Complex of carboxyl group and ammonium cation with Cl^- counterion)

Formation of this complex is characterized with very high gain in energy ($\Delta E = 526.288$ kJ/mol). The length of O–H bond in carboxyl group increases from 0.969 to 2.050 Å, whereas the distance between Cl^- anion and the proton of carboxyl group is 1.83 Å. For comparison, the length of H–Cl bond in HCl molecule is 1.28 Å. The distance between Cl^- ion

and the proton of ammonium cation has been found to be 3.11 Å.

In this way, the chlorine counterion draws off the proton from the carboxyl group in the structure outlined by model 13. It should be noted that the position of chlorine counterion with respect to the carboxyl group and ammonium cation governs both the complexation energy and the location of the proton separated from corresponding functional groups. If the Cl^- ion is located in vicinity of ammonium cation, it tears away the proton from the ammonium group. As the Cl^- anion is located adjacent to the carboxyl group, it induces disengagement of the proton from carboxyl anion. Thus the results of quantum chemical calculations, which reveal the existence of a wide variety of the complexes with a structures similar to the model 13 and close values of the complexation energy, provide an explanation for the broad and complex profile of the band of N–H bond stretching vibrations in FTIR spectra of PDMAEMA-*co*-MMA/BMA polycation and its blends with PMAA-*co*-EA polyacid shown in Figure 10.

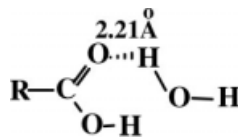
The interaction mechanism described by model 13 underlies the formation of free protons from the carboxyl groups of polyacid under action of ammonium polycation (see reaction (2) and Figure 11). Because the pioneer works of Kabanov and Zezin in 1970th, it was thought that the reaction (3) has no precedent in low molecular weight chemistry and provided by the cooperative mechanism of interaction of the functional groups in side chains of polymer.^{25,40} However, the quantum chemical calculations presented above predict the occurrence of exchange reaction (2) for low molecular weight compounds bearing carboxyl groups and ammonium cations in their molecules. To check this prediction and confirm applicability of the models presented in Figure 1, we have performed potentiometric titration of isobutyric acid (IBA) with hydrochloride of *N,N*-dimethylisopropyl amine (DMPA), which can be regarded as low molecular weight analogs of monomeric methacrylic acid and *N,N*-dimethylaminoethyl methacrylate units in the studied polyelectrolytes. The results are presented in Figure 14.

As is seen from Figure 14, the exchange reaction (2) is typical not only of polyacid titration with polycation solution, but the titration of low molecular weight acid by low molecular weight ammonium cation. In low molecular weight analogues of polyacid and polycation monomer units the drop of pH is less pronounced that can imply not only the contribution of cooperative effect, but also the difference in pK of the analyte and titrant solutions. In this way, independent data of potentiometric titration confirm the validity of quantum chemical calculations for comparative analysis of the strength of molecular interactions in polybase–polyacid blends.

Molecular Interactions in the Presence of Absorbed Water

As has been earlier shown in our recent publication,³¹ inclusion of water molecules into hydrogen bonding between functional groups of PVP, PEG and PMAA-co-EA leads to significant bond enhancement. In this work we consider the effect of water molecules on hydrogen and ionic bonding between complementary polyelectrolytes, such as PDMAEMA-co-MMA/BMA polybase and PMAA-co-EA polyacid.

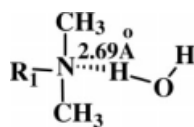
Carboxyl group of the model 1 gives comparatively loose associates with water. Most energetically favorable is the complex with the length of hydrogen bond of 2.21 Å, which is formed because of interaction of carbonyl oxygen atom with one proton of water molecule ($\Delta E = 22.605$ kJ/mol, model 14).



Model 14 (Complex of carboxyl group with water)

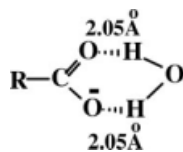
Other associates of the carboxyl group with a single or few water molecules are less stable.

The complex of aminogroup (model 3) with water (model 15) is characterized with lower formation energy ($\Delta E = 12.340$ kJ/mol):



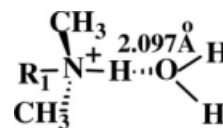
Model 15 (Complex of aminogroup with water)

Carboxylate anion (model 2) forms with water a number of stable complexes with different angles of the turn of water molecule relative to the plane of $O=C-O^-$ anion. Most energetically stable is symmetric complex illustrated by model 16, where both water protons form short bonds to different oxygen atoms of the anion ($\Delta E = 64.273$ kJ/mol):



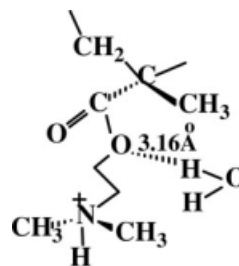
Model 16 (Complex of carboxylate anion with water)

Ammonium cation (model 4) forms with water molecule a complex outlined by model 17 ($\Delta E = 47.587$ kJ/mol):

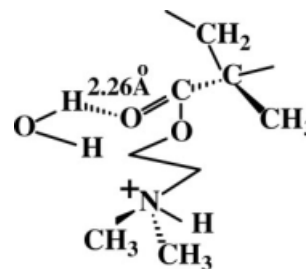


Model 17 (Complex of ammonium cation with water)

Water molecules are also capable of forming the stable H-bonded complexes with oxygen atom of the ester group in the side chains of PDMAEMA-co-MMA/BMA polybase (model 18, $\Delta E = 34.810$ kJ/mol and model 19, $\Delta E = 31.288$ kJ/mol):



Model 18 (Complexes of ester group of ammonium cation with water)

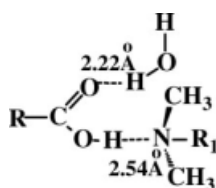


Model 19

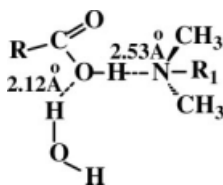
Similar complexes are also found for the ester group of uncharged amine (model 3) with water, however in this case the gain in energy under complex formation is lower than for models 18 and 19.

As follows from the results presented in this section, complex formation with water for ammonium cation and carboxyl anion is accompanied with a greater gain in energy than the complex formation of uncharged amine and carboxyl group. The energy of complex formation with water for carboxyl anion is by 4 kJ/mol higher than for ammonium cation.

We will now consider the effect of absorbed water on the interaction between amino and carboxyl groups. Inclusion of water molecule into the complex between uncharged carboxyl group and aminogroup (model 5) produces two types of structures, model 20 ($\Delta E = 37.938$ kJ/mol) and model 21 ($\Delta E = 42.894$ kJ/mol):



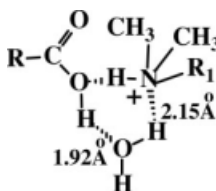
Model 20 (Ternary complexes of uncharged carboxyl group, aminogroup and water)



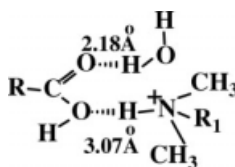
Model 21

The energy of ternary complex formation is insignificantly increased in comparison with binary complex (model 5, $\Delta E = 26.195$ kJ/mol), and the length of H-bond between nitrogen atom of aminogroup and the proton of carboxyl group becomes shorter. The length of hydrogen bond between oxygen atoms of carboxyl group and the proton of water is appreciably shorter than hydrogen $N\cdots H$ bond in the complexes. This finding is in reasonable agreement with our earlier observation that the length of $-O\cdots H$ bond is always shorter than the length of $N\cdots H$ bond.

The complex of carboxyl group with ammonium cation (model 6) gives with water two types of associates, model 22 ($\Delta E = 67.10$ kJ/mol) and model 23 ($\Delta E = 152.43$ kJ/mol).



Model 22 (Ternary complexes of uncharged carboxyl group, ammonium cation and water)



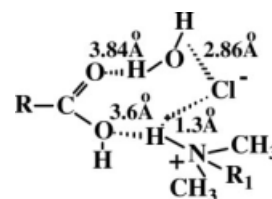
Model 23

Ternary complex outlined by model 22 ($\Delta E = 67.10$ kJ/mol) is significantly less stable than the binary complex (model 6, $\Delta E = 114.00$ kJ/mol). In contrast, inclusion of water molecule into the struc-

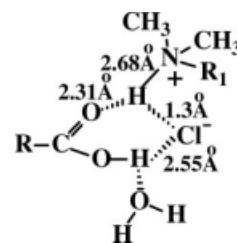
ture of binary complex between carboxyl group and ammonium cation (model 6) leads to the gain in complex formation energy ($\Delta E = 152.43$ kJ/mol against 114.0 kJ/mol).

Concurrent Effect of Inorganic Counterions and Water Molecules

Interaction of ternary complex formed by carboxyl group, ammonium cation and water molecule (model 23) with chlorine counterion increases dramatically the gain in energy under complex formation, leading to the complexes described by model 24 ($\Delta E = 638.18$ kJ/mol) and model 25 ($\Delta E = 650.23$ kJ/mol):

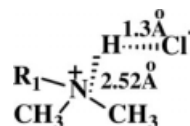


Model 24 (Ternary complexes of uncharged carboxyl group, ammonium cation and water in the presence of chlorine counterion)



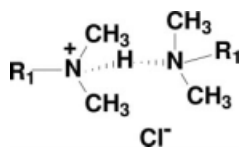
Model 25

As follows from the results of quantum chemical calculations, if inclusion of water molecule into the structure of complex does not necessarily increase the energy of complex formation, effect of chlorine counterion invariably leads to much more energetically favorable complexes. Ammonium cation (model 4) has sufficiently high ionization potential of 7.1 e.V. (681.0 kJ/mol). In the presence of chlorine counterion the complex outlined by model 26 is formed ($\Delta E = 590.33$ kJ/mol), where Cl^- ion attracts significantly the proton from nitrogen atom:



Model 26 (Interaction of ammonium cation with chlorine counterion)

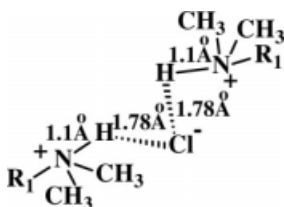
As has been shown above, uncharged aminogroup can form a stable complex with its own cation (model 12, $\Delta E = 46.765$ kJ/mol). In the presence of chlorine counterion the energy of such complex formation increases to 421.02 kJ/mol (model 27):



Model 27 (Complex of uncharged aminogroup with ammonium cation tightened by chlorine counterion)

The lengths of N^+-H and $H-N$ bonds in this complex are found to be 1.069 and 1.80 Å, respectively.

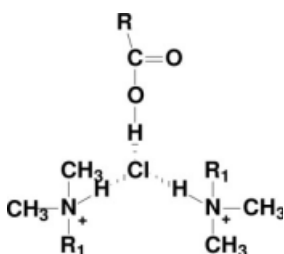
Much more energetically favorable is dimeric complex of two ammonium cations characterized by model 28 ($\Delta E = 666.48$ kJ/mol) where the protons are confined to the nitrogen atoms of cation:



Model 28 (Dimeric complex of two ammonium cations with chlorine counterion)

Water molecules do not affect appreciably the structure and formation energy of the complexes described by models 26, 27, and 28.

Interaction of uncharged carboxyl group of polyacid with dimeric complex of two ammonium cationic groups in the presence of chlorine counterion (model 28) results in the formation of most energetically favorable complex described by model 29, $\Delta E = 689.46$ kJ/mol:

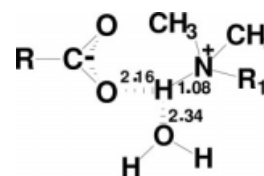


Model 29 (Complex of uncharged carboxyl group with two ammonium cations and chlorine counterion)

In contrast, interaction of carboxyl group with a complex of uncharged aminogroup and ammonium cation in the presence of chlorine anion (model 27) results in decomposition of the complex and HCl formation.

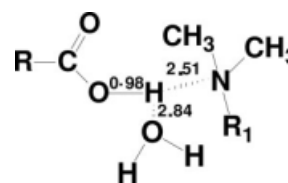
Let us consider now the effects of water and chlorine counterions on the characteristics of ionic cat-

ion-anion complexes. Molecules of water and chlorine counterion affect both geometric parameters and formation energy of hydrogen-bonded complexes of carboxylate anion with ammonium cation (see model 7, $\Delta E = 257.50$ kJ/mol). Inclusion of water molecule into H-bonding results in the formation of much more energetically favorable complexes outlined by models 29 ($\Delta E = 513.00$ kJ/mol) and 30 ($\Delta E = 593.06$ kJ/mol). In model 30, the proton of ammonium cation forms simultaneously two hydrogen bonds with oxygen atoms of carboxylate anion and water.



Model 30 (Ternary H-bonded complex of ionized carboxyl group, ammonium cation and water)

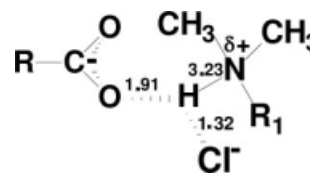
In model 31 full proton transfer occurs from the ammonium cation to the carboxyl anion, and the proton holds two H-bonds to nitrogen atom of parent ammonium cation and oxygen atom of water molecule.



Model 31 (Ternary charge transfer complex of ionized carboxyl group, ammonium cation and water)

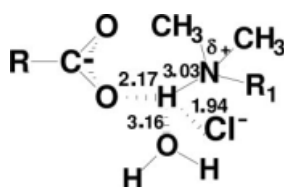
As a result of proton transfer, this complex has a composition similar to chemical composition of the complexes formed by uncharged carboxyl group, uncharged aminogroup and water (see models 20 and 21). However the energy of charge transfer complex formation (593.06 kJ/mol) is incomparably greater than complexation energies of initially non-ionized components (38–43 kJ/mol).

In the presence of chlorine counterion, waterless H-bonded complex of carboxylate anion with ammonium cation (model 32) is characterized with very high formation energy ($\Delta E = 644.02$ kJ/mol).



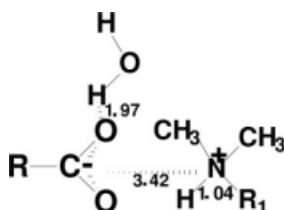
Model 32 (Hydrogen bonded complex of carboxylate anion and ammonium cation, stabilized with chlorine counterion)

Inclusion of water molecule into the structure of this complex results in some decrease of complexation energy (model 33, $\Delta E = 524.04$ kJ/mol):



Model 33 (Ternary H-bonded complex of ammonium cation with carboxylate anion and water in the presence of chlorine counterion)

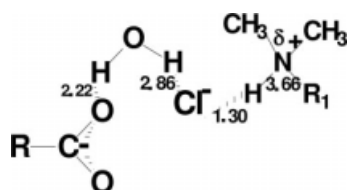
Among cation-anion complexes based on ionic bonding (model 8), most strong is the complex with water (model 34).



Model 34 (Ternary ionic complex of ammonium cation with carboxylate anion and water)

In this case, the complexation energy is 424.93 kJ/mol that is about 20 kJ/mol higher than the energy of corresponding waterless complex (model 8, $\Delta E = 404.363$ kJ/mol).

In the presence of chlorine counterion, another very strong complex is formed (model 35, $\Delta E = 638.18$ kJ/mol):



Model 35 (Ternary ionic complex of ammonium cation with carboxylate anion and water in the presence of chlorine counterion)

In this complex, the proton of ammonium cation shifts from the nitrogen atom to chlorine anion, whereas water molecule forms two H-bonds with oxygen atom of carboxyl anion and chlorine anion. No appreciable interaction has been found between the carboxyl anion and the complexes of ammonium cation with uncharged aminogroup or another ammonium cation in the presence of chlorine anion (models 27 and 28).

In real systems, the presence of carboxyl anion in blend is usually associated with availability of corresponding counterion that is typically sodium cation.

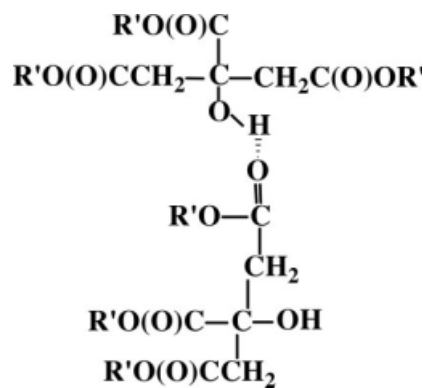
As quantum chemical calculations have shown, in the presence of two counterions, chlorine and sodium, their interaction to a great extent inhibits enhancing effect of chlorine counterion.

The results of quantum chemical calculations presented in this article provide an insight into attribution of a variety of bands observed in FTIR spectra of PDMAEMA-co-MMMA/BMA polybase blends with PMAA-co-EA polyacid. As an example, the band at 2600–3100 cm^{-1} in FTIR-spectrum of ammonium polycation blends with polyacid (Fig. 10) may be attributed to the complexes described by models 13, 23, 24, and 25. A fact that complexes 13, 24, and 25 demonstrate close values of formation energy is most likely responsible for appreciable breadth and nonuniform profile of this band.

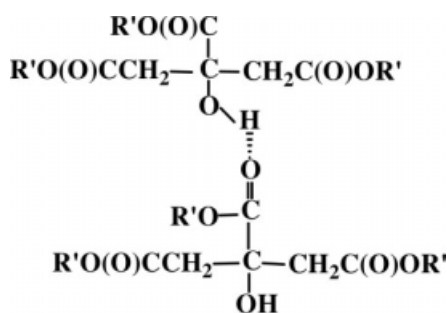
Interaction of TEC Plasticizer

Models 1–35 considered above relate to interaction between functional groups of polybase and polyacid. To impart the properties of pressure sensitive adhesives to polyelectrolyte complexes, they should be mixed with appropriate plasticizer, typically TEC. As has been shown in the discussion around Figure 13 of this article, FTIR-spectra demonstrate interaction of hydroxyl group in TEC molecule with macromolecules of polyelectrolytes in blends. Quantitative insight into molecular mechanisms of TEC interaction with amino groups of polybase, carboxyl groups of polyacid and as well as self-association of TEC molecules is obtained with quantum chemical calculations.

As our calculations have shown, TEC molecules are capable of forming a wide range of hydrogen-bonded self-associates with participation of $-\text{OH}$ and $-\text{COOR}'$ groups ($\text{R}' = \text{C}_2\text{H}_5$). Energy of such complex formation is rather low (3–15 kJ/mol), but the number of the complexes is very high. Models 36 and 37 present typical examples of such low energy complexes.

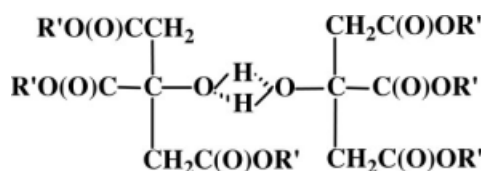


Model 36 (H-bonded self-associates of TEC molecules)



Model 37

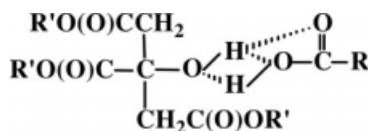
Most energetically favorable is self-associate of TEC molecules with a structure illustrated by model 38, $\Delta E = 44.671$ kJ/mol:



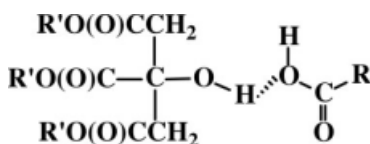
Model 38 (H-bonded dimer of TEC molecules)

The lengths of hydrogen bonds in this complex are 2.22 and 2.78 Å.

The complexes of TEC with carboxyl group of polyacid (models 39 and 40) have similar energies of formation ($\Delta E = 41.497$ and 47.569 kJ/mol, respectively):



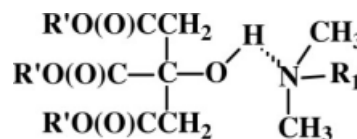
Model 39 (H-bonded TEC complexes with carboxyl group)



Model 40

It is notable that complex 38, which has some lower complexation energy involves three H-bonds (2.15, 2.22 and 2.68 Å). Comparatively, more stable complex 40 is formed by a single hydrogen bond.

H-bonded complex of TEC with aminogroup (model 41) is characterized with lower formation energy ($\Delta E = 19.734$ kJ/mol):



Model 41 (H-bonded complex of TEC with aminogroup)

Ternary complexes of TEC molecule with carboxyl and amino groups are characterized with negligible formation energies (about 10 kJ/mol). Thus the results of quantum chemical calculations are in good agreement with FTIR data that exhibit comparatively weak TEC interaction with functional groups of polyelectrolytes.

Ranking Mechanisms of Interpolymer Bonding on Complexation Energies

In Table V the results of calculations are arranged in descending order of the complexation energy.

Among all the studied structures, most energetically favorable is an associate of uncharged carboxyl group of polyacid with two ammonium cations of completely protonated polybase which are held together with chlorine counterion serving as a binder ($\Delta E = 689.46$ kJ/mol). Dimeric complex of two ammonium cations in the presence of chlorine anion is also very stable ($\Delta E = 666.48$ kJ/mol). This fact implies strong inclination of chlorine anion towards ammonium cations that makes it possible to overcome Coulomb electrostatic repulsion between two cations. Indeed, interaction energy between ammonium cation and chlorine counterion is assessed to be 590.33 kJ/mol. In this connection it comes as no surprise that the majority of the complexes between ammonium cation and carboxylate anion (or uncharged carboxyl group), coupled with chlorine anion, are characterized with very high complexation energy (in the range from 520 to 650 kJ/mol).

Mechanisms of molecular interaction between carboxyl group of polyacid and aminogroup (or ammonium cation) in polybase follow three types of chemical reactions:

1. Neutralization reaction leading to the formation of hydrogen bonded polybase-polyacid complexes;
2. Exchange reaction between ammonium cation and uncharged carboxyl group resulting in the formation of strong inorganic acid (HCl) from ammonium salt of polybase and weak carboxyl-containing polyacid;
3. Reaction of charge neutralization between ammonium salt of polybase and ionized carboxyl groups of polyacid.

As is evident from Table V, ionic complexes resulting from charge neutralization reaction (3) are

TABLE V
Comparative Strength of Ionic and Hydrogen Bonding Between Amino Groups of Polybase, Carboxyl Group of Polyacid and Hydroxyl Group of Plasticize

Complex type	Complex structure	Formation energy (kJ/mol)
Complex of uncharged carboxyl group with two ammonium cations and chlorine counterion		689.46
Dimeric complex of two ammonium cations with chlorine counterion		666.48
Ternary complex of uncharged carboxyl group, ammonium cation, and water in the presence of chlorine counterion		650.23
Hydrogen bonded complex of carboxylate anion and ammonium cation, stabilized with chlorine counterion		644.02
Ternary ionic complex of ammonium cation with carboxylate anion and water in the presence of chlorine counterion		638.18
Ternary complex of uncharged carboxyl group, ammonium cation and water in the presence of chlorine counterion		638.18

TABLE V Continued

Complex type	Complex structure	Formation energy (kJ/mol)
Ternary charge transfer complex of ionized carboxyl group, ammonium cation, and water		593.06
Interaction of ammonium cation with chlorine counterion		590.33
Complex of uncharged carboxyl group and ammonium cation with Cl ⁻ counterion		526.29
Ternary H-bonded complex of ammonium cation with carboxylate anion and water in the presence of chlorine counterion		524.04
Ternary H-bonded complex of ionized carboxyl group, ammonium cation and water		513.00
Ternary ionic complex of ammonium cation with carboxylate anion and water		424.93
Complex of uncharged aminogroup with ammonium cations tightened by chlorine counterion		421.02
Ionic complex of carboxylate and ammonium counterions		404.36

TABLE V Continued

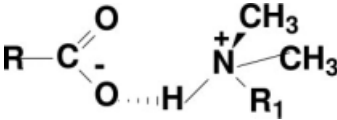
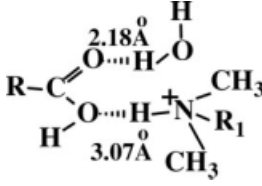
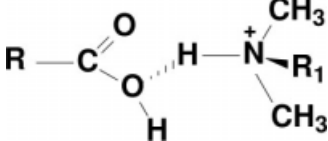
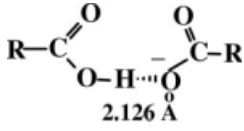
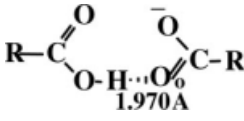
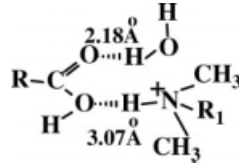
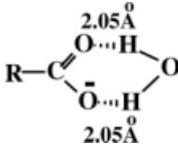
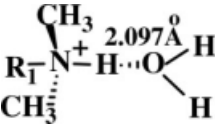
Complex type	Complex structure	Formation energy (kJ/mol)
H-bonded complex of carboxylate and ammonium ions		257.50
Ternary complex of uncharged carboxyl group, ammonium cation, and water		152.43
H-bonded complex of uncharged carboxyl group with ammonium cation		114.00
Complexes of carboxyl group and carboxylate anion		89.91
		73.51
Ternary complex of uncharged carboxyl group, ammonium cation, and water		67.10
Complex of carboxylate anion with molecule of water		64.27
Complex of ammonium cation with molecule of water		47.59

TABLE V Continued

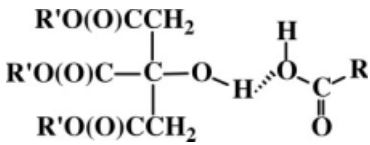
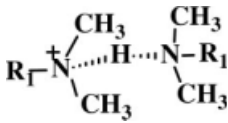
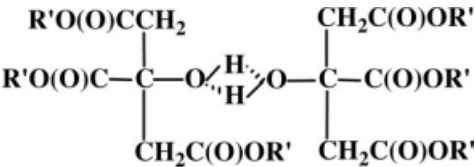
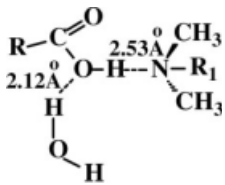
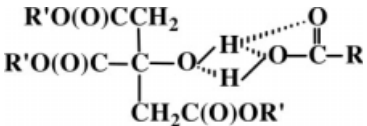
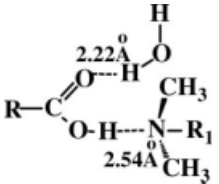
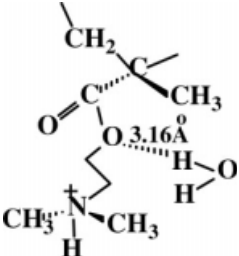
Complex type	Complex structure	Formation energy (kJ/mol)
H-bonded TEC complex with carboxyl group		47.57
Associate of ammonium cation with uncharged aminogroup		46.77
H-bonded dimer of TEC molecules		44.67
Ternary complex of uncharged carboxyl group, aminogroup, and water		42.89
H-bonded TEC complex with carboxyl group		41.50
Ternary complex of uncharged carboxyl group, amino-group, and water		37.94
Complex between ester group of ammonium cation with water		34.81

TABLE V Continued

Complex type	Complex structure	Formation energy (kJ/mol)
Complex between ester group of ammonium cation with water		31.29
Self-associate of carboxyl groups		26.48
H-bonded complex between uncharged amino and carboxyl groups		26.20
Complex of carboxyl group with water		22.61
H-bonded complex of TEC with aminogroup		19.73
Complex of aminogroup with water molecule		12.34

typically much stronger than the H-bonded complexes produced by neutralization reaction between uncharged amino and carboxyl groups (1). The strength of complexes obtained with exchange reaction (2) approaches the value typical of ionic complexes ($\Delta E = 526.29$ kJ/mol, model 13).

Exchange reaction (2) has been earlier declared to occur as a result of cooperative interaction between functional groups disposed in monomeric units of complementary polymer chains and there is no such precedent in the chemistry of low molecular weight compounds.^{25,40} However, as established above, this

reaction proceeds also between low molecular weight carboxylic acids and ammonium cations. Typical example of this reaction is the complex of uncharged aminogroup with ammonium cation ($\Delta E = 46.77$ kJ/mol, model 12). In the presence of chlorine anion the formation of such complex becomes much more energetically favorable ($\Delta E = 421.02$ kJ/mol, model 27). The existence and stability of such complexes indicate that ammonium cation behaves as an acid in the complex with uncharged aminogroup (base). If we follow traditional definition of acid as a proton-donating substance and a base as a proton accepting matter, the implication of exchange reaction (2) is that the $\text{HN}^+(\text{CH}_3)_2^-$ group is appreciably stronger acid than carboxyl COOH group. This means also that in PDMAEMA-MMA/BMA blends with PMAA-co-EA the aminogroup-containing polymer is not necessarily polybase, but in protonated form it should be considered as polyacid with respect to nonprotonated form.

As follows from the data presented in Table V, proton-donating capability of functional groups in the studied polyelectrolyte blends diminishes in the order: $\text{HN}^+(\text{CH}_3)_2^- > \text{HOOC}- > \text{HO}-$. Proton-donating capacity can be significantly improved in the presence of Cl^- ions, the effect of which can be inhibited if Na^+ cations are available in the blend or solution. Inhibiting action of sodium cations on proton-donating capacity of carboxyl groups in the presence of chlorine counterions underlies molecular nature of well-known Donnan effect which states that electrostatic interactions in polyelectrolytes become weaker in the media with high ionic strength.⁴⁴ Proton-accepting capability weakens in the order: uncharged aminogroup $>$ carboxylate anion $>$ uncharged carboxyl group (bearing two proton-accepting oxygen atoms in carbonyl and hydroxyl groups) $>$ hydroxyl group (of TEC plasticizer).

Most strong ionic complexes of ammonium cation with carboxylate anion or uncharged carboxyl group involving chlorine anion as a binder are followed in Table V by ternary H-bonded acid-base complexes associated with molecule of water. They have somewhat lower complexation energy (420–520 kJ/mol). As has been shown in our earlier publication,³¹ molecules of absorbed water are capable to stabilize essentially the hydrogen-bonded complexes. In ionic complexes this stabilizing effect is not so well pronounced. In the absence of chlorine anion and water molecules, both ionic and H-bonded acid-base complexes have comparatively lower energy of complex formation. Thus, ionic complex of carboxylate anion and ammonium cation is appreciably more stable (404 kJ/mol) than their H-bonded complex (257.5 kJ/mol). H-bonded complex of uncharged carboxyl group and ammonium cation is characterized with much lower complexation energy (114 kJ/mol).

Lastly, H-bonded complex between uncharged amino and carboxyl group is comparatively weaker (26 kJ/mol, Table V).

Another conclusion following from the data presented in Table V is that multi-component complexes are generally stronger than binary associates. Similar observation was also made in our earlier article describing molecular interactions in PVP-PEG-PMAA-co-EA-water blends.³¹ However, the results of present research demonstrate that this finding is not due to a large number of hydrogen and ionic bonds in ternary and four-component complexes. As has been shown above, the complex of the same composition provided by single hydrogen bond can be much stronger than the complex of another geometry involving few hydrogen bonds.

CONCLUSIONS

Molecular design of new polymer materials with tailored performance properties requires knowledge of quantitative structure–property relationship. For rational development of pressure-sensitive adhesives based on polyelectrolyte complexes, insight is needed into mechanisms of molecular interaction between complementary functional groups of polybase and polyacid macromolecules. FTIR-spectroscopy allows identification of interacting functional groups in the polyelectrolyte blends. A model polyelectrolyte system considered in this study includes a polybase, a copolymer of *N,N*-dimethylaminoethyl methacrylate with methylmethacrylate and butylmethacrylate (PDMAEMA-MMA/BMA), a polyacid, a copolymer of methacrylic acid with ethylacrylate (PMAA-co-EA), and a plasticizer, triethylcitrate (TEC). This model system possesses unique viscoelastic and adhesive properties, coupled with water-absorbing capacity, which underlie its practical usage.

To evaluate the structure and formation energies of the variety of interpolymer complexes that involve both hydrogen and ionic bonding, quantum-chemical calculations have been performed. The results of quantum chemical calculations facilitate appreciably the interpretation of FTIR-spectra. Thus, they provide an explanation for the width and indented profile of several bands in FTIR-spectra indicating that this effect results from a variety of complex structures and proximity of interaction energies between the same functional groups of complementary macromolecules. Comparison of the molecular mechanisms of polybase-polyacid interaction on the values of complexation energies gives an insight into most energetically favorable interaction mechanisms between complementary functional groups of the polymers in blends. The functional groups in our model system are typical of variety of polyelectrolytes that motivates fundamental

significance of obtained results for the science of polyelectrolyte complexes.

The impact of key mechanisms of molecular interactions between the functional groups of complementary polyelectrolyte macromolecules and plasticizer on phase state, viscoelastic properties and adhesion of PDMAEMA–MMA/BMA blends with PMAA-co-EA and TEC plasticizer will be discussed in our subsequent publications.

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