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Solution and Solid State Behavior of Poly(N-Acetyliminoethylene)-Poly(Methacrylic Acid) Interpolymer Complexes

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SOLUTION AND SOLID STATE BEHAVIOR OF POLY(N-ACETYLIMINOETHYLENE) - POLY(METHACRYLIC ACID) INTERPOLYMER COMPLEXES

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ABSTRACT

A thorough comparative study of poly(N-acetyliminoethylene)-poly(methacrylic acid) blends, corresponding synthetic complexes and template complexes was performed. The experimental data, obtained from DSC, TGA, X-ray diffraction, viscometric and turbidimetric determinations, showed the dependence of the solution and solid state properties of the studied systems, not only on their structural features

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but also on the adopted preparative approach. The different degrees of orientation of groups involved in interpolymer hydrogen bonding interactions yielded a higher thermal stability for template complexes as compared to the other studied polymeric materials.

The possibility of transforming the physical interpolymer bonds into chemical ones through a transamidation reaction was evidenced.

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INTRODUCTION

In recent years, the interpolymer complexes has become one of the most studied subjects in macromolecular chemistry. The increased interest in this field is due to the possible compatibility of intermolecular interactions to polymer blends [1-3], in molecular recognition directed organic synthesis, or to facilitate some intermacromolecular reactions [4].

Numerous reports are devoted to the interpolymer complexes stabilized by hydrogen bonds. Most of them are based on poly(carboxylic acids) and nonionic macromolecules, homo - or copolymers containing hydrogen bond acceptor units (i.e.,poly(ethylene glycol) [5], (co)poly(vinyl ethers) of glycols [6], poly(vinylpyrrolidone) [7], poly(vinyl alcohol) [8,] poly(N-propionyl iminoethylene) [9,] poly(propylene glycol) [10]).

This paper presents some observations on the solution and solid state interactions in poly(N-acetyliminoethylene) (PNAI) - poly(methacrylic acid) (PMAA) systems, results of a systematic comparative study performed on the corresponding blends, polymeric template complexes and synthetic complexes. Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), X-ray diffraction analysis and viscometry were the experimental techniques used to distinguish the differences between their behavior peculiarities in relation to sample preparation procedure.

EXPERIMENTAL

Materials

Poly(N-acetyliminoethylene) (PNAI) oligomers were synthesized by living cationic polymerization of 2-methyl-2-oxazoline initiated with1,4-dibromo-2-butene [11] followed by the hydrolysis of the brominated end groups in the presence of

K_2CO_3. Poly(methacrylic acid) (PMAA) was obtained by solution polymerization in toluene, at 60°C, with benzoyl peroxide as initiator. Its viscosity average molecular weight was determined in methanol at 26°C [12].

Films of polymer blends were prepared by solution casting (solvent: dimethylformamide) onto glass plates. After solvent evaporation, (T = 50°C) the films were dried under vacuum at 60 °C for 7 days, ground into powders, and examined.

The macromolecular complexes were prepared by two methods:

a) the mixing method (synthetic complexes) and

b) the polymerization method (template polymerization).

Synthetic complexes were obtained by joint precipitation at room temperature using initial 1% aqueous solutions of PNAI (M_n = 7800) and PMAA (M_v = 150000). The PMAA solution was added, dropwise, under stirring, into the PNAI solution. The precipitates then were filtered (G_3), washed several times with water to remove the final existing free PNAI and/or PMAA, and then dried in vacuum to constant weight (T = 60°C). The low drying temperature was chosen to avoid inadvertent anhydride formation from carboxyl groups.

Template complexes were synthesized by methacrylic acid (MAA) polymerization in the presence of PNAI templates. The radical active species were generated through the thermolysis or photolysis of 4,4-azobis-4-cyanopentanoic acid (ACP) or PNAI macroazoinitiators [13] obtained by coupling α,ω,-dihydroxy-poly(N-acetyliminoethylene)s of controlled molecular weights with 4,4-azobis(4-cyanopentanoyl chloride). The 4,4-azobis-4-cyanopentanoic acid was used after preliminary drying.

The polymerizations were carried out in sealed glass or quartz ampoules, under argon, under the conditions mentioned in Table 1. A high pressure mercury lamp of 500 W, situated at 16 cm from the ampoules, was used as a irradiation source for the photochemical polymerization.

The products were washed repeatedly with methylene chloride in order to remove the unscissed PNAI macroinitiator or the excess of PNAI template.

Compositions of template and synthetic complexes, determined by elemental analysis of nitrogen, are listed in Table 1. The proposed structure [14] of the complexes (see the Results and Discussion section) is presented in Figure 1. The specific propagation in template polymerizations (*zip* - type mechanism) is expected to lead to an increased order of chains packing as compared to mutual composition.

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TABLE 1. Preparation Procedure and Composition of PMAA-PNAI Samples

Code	N%	[PMAA/PNAI] mol/mol	Preparative Method
M_{1-8}		0.1; 0.33; 0.66; 0.75; 1; 2; 3; 9	blends casted from the mixture of 1% solutions in DMF $M_{vPMAA} = 150000$; $M_{nPNAI} = 7800$
P*	6.4-6.7	1.4 - 1.6	synthetic complex mutual precipitation from 1% aqueous solutions $M_{v\ PMAA} = 150000$; $M_{n\ PNAI} = 7800$
T_1	6.4	1.55	template polymerization; $[MAA]_0 = 0.5$ m, [T]/[M] = 1
T_2	7.6	1.2	T = PNAI oligomer, $M_{n\ PNAI} = 7800$, [ACP] = 2% with respect to monomer, 72°C, 1 hour
T_3	6.1	1.8	block copolymer, template polymerization; [MAA] = 1 m, [T]/[M] = 1, T = PNAI macroinitiator with inserted sequences of DP = 21, 72°C, 5 hours
T_4	9.4	0.7	block copolymer, template polymerization; $[MAA]_0 = 0.5$ m, [T[/[M] = 1, T = PNAI macroinitiator with inserted sequences with DP = 21, 80 °C, 5 hours.
T_5	6.5	1.5	block copolymer, template polymerization; $[MAA]_0 = 3$ m, [T]/[M]= 1/3, T = macroinitiator with inserted PNAI sequences of DP = 21, 70°C, 5 hours
T_6	4.6	2.6	T = macroinitiator with inserted PNAI sequences of DP = 21, 70°C, 5 hours
T_7	6.6	1.5	DP = 58
T_8	6.1	1.7	DP = 75
TP_1	7.4	1.2	block copolymers, photochemical polymerization $[MAA]_0 = 0.4$ m; [T]/[M] = 1
TP_2	5.2	2.1	T = macroinitiator with inserted PNAI sequences of $M_{n\ PNAI} = 7800$, 1 h.our

* Almost all synthetic complexes resulted by the precipitation of PMAA and PNAI aqueous solution for different mixture compositions are characterized by a value of 1.5 for the PMAA :PNAI molar ratio.

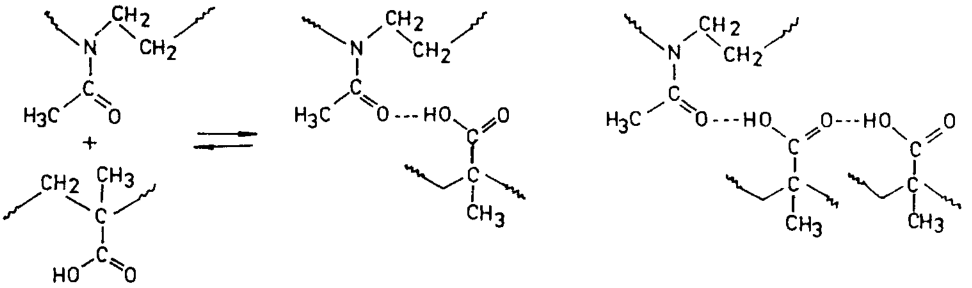

Figure 1. Schematic representation of the interpolymeric PMAA-PNAI complexes.

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Characterization

Viscometric measurements were carried out with an Ubbelohde viscometer for different PMAA/PNAI mixtures with various compositions and polymer molecular weights. Each determination was performed after 30 minutes of solution mixing, the time required for complex stabilization. TGA data was obtained with a Paulik-Paulik-Erdey derivatograph (MOM Budapest) (powder form samples, obtained either directly or through grounding, 50 mg, N_2 atmosphere, heating rate 12°C/min). IR (KBr pellets) spectra were registered on a Specord M-40 spectrophotometer.

Glass transition temperatures were determined by differential scanning calorimetry using a DSC Seiko 220 C apparatus, at a heating rate of 10°C/min, under N_2 atmosphere. For the polymer blends, the first scan was registered in the temperature range of 20-230°C, in order to remove any trace of solvent. The results obtained were found to be similar to those yielded after a first run carried out in the 20-130°C range. For the template complexes, preliminary measurements evidenced a greater heating sensibility, so that the first run for water removal was performed only until 130°C to prevent dehydration. Usually, the second scan (in the temperature range 20-250°C) was considered for the determination of glass transition temperatures.

For the X-ray diffraction study, the powder samples were analyzed with an INEL CPS 120 X-ray camera using $K\alpha_1$ radiation of Cu.

The turbidimetric measurements were performed with an FEK-M type photocolorimeter.

RESULTS AND DISCUSSION

The presence of the tertiary amide group in the molecular structure of the polymers studied includes the poly(N-acyliminoethylene)s in the class of hydrogen bonding acceptors. Preliminary data reported by Pearce and Kwei [9] on poly(N-propionyliminoethylene) behavior shows the strong tendency of this compound to engage intermolecular hydrogen bonding with polymers containing carboxyl or hydroxyl groups. The capacity of poly(N-acyliminoethylene) to form more than one complex with PMAA, with different compositions, depending on solvent nature and feed ratio, was noted as a peculiarity [9.] The following data deal with the PMAA - PNAI complexes formed in aqueous solution.

Solution properties

Viscometric measurements

Polymer complexes can easily be studied by determining the maximum or, more often, minimum reduced viscosity against weight composition for complexation of the presynthesized complementary polymers. Earlier investigations on the PMAA-PNAI system revealed that water and alcohols are more appropriate solvents for a complexation study as compared to, e. g., DMF [15]. Thus, extensive complexation experiments were carried out in water in order to establish the best composition ratio for the PMAA-PNAI polycomplex and the factors of influence.

Figure 2 shows the dependence of the reduced viscosity of the aqueuos solutions of PMAA-PNAI mixtures, with various PNAI or PMAA chain lengths, on the weight ratio of the components.

The visible deviation from additivity is evidence of strong polymer interactions occurring with the formation of compact complex particles. As can be seen, the complexation is possible even for PNAI oligomers with average molecular weights as low as $M_n = 560$ (Figure 2). Complex stoichiometry is strongly influenced by mixture composition and by the chain length of the partners. Specific for the here studied PNAI-PMAA pair is the presence of more than one extreme in the η_{red} - mixture composition curves. The data suggest the formation of more than one stable complex, in accordance with the earlier data reported by Kwei and Pearce for the poly(N-propionyliminoethylene) - PAA (poly(acrylic acid)) system [9]. This peculiar behavior intensifies with the increase of the length of the two partners (Figure 2b). In the high PNAI oligomers concentration range the η_{red} - composition graphs show a positive deviation from additivity. This might be explained by the formation of a tridimensional structure due to intermacromolecular bonding of the

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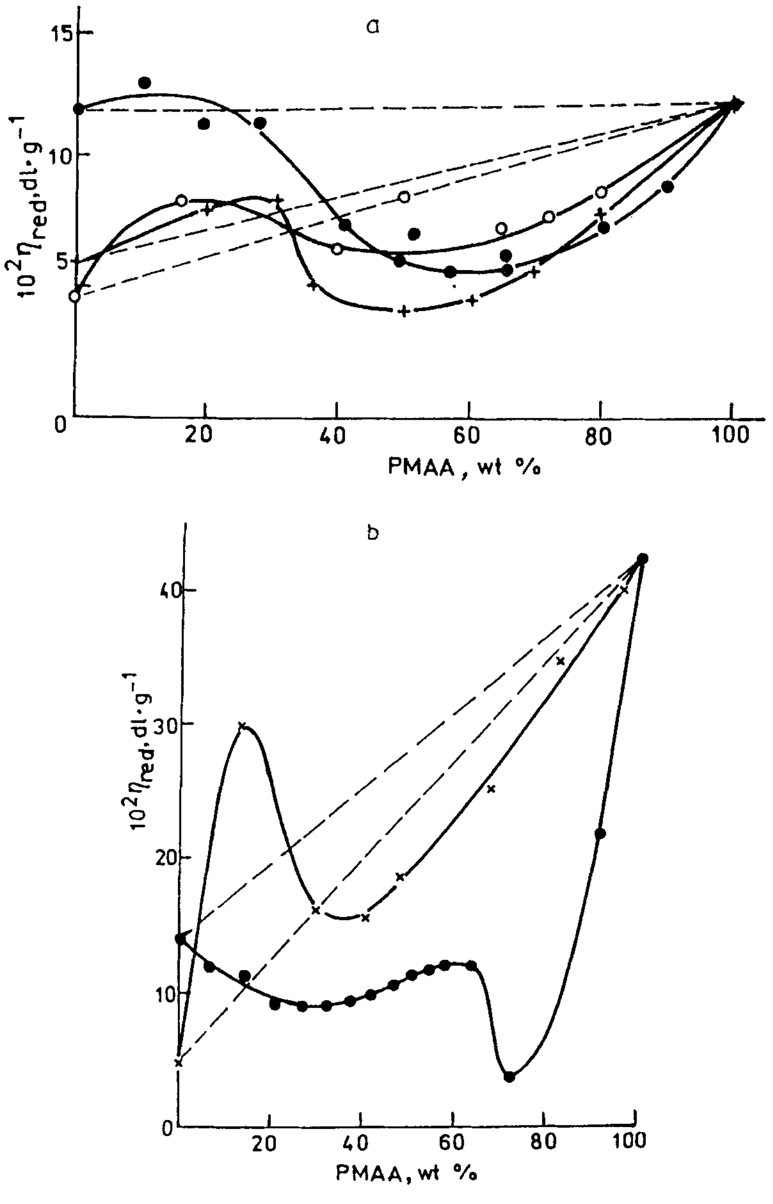

Figure 2. Plots of η_{red} vs. the PMAA weight percent for the aqueous solutions of PMAA-PNAI mixtures (c = 0.5 g·dl^{-1}).

a. M_v PMAA = 10890
(o) M_n PNAI = 560
(x) M_n PNAI = 5200
(•) M_n PNAI = 7000

b. M_v PMAA = 150000
(x) M_n PNAI = 560
(•) M_n PNAI = 7800

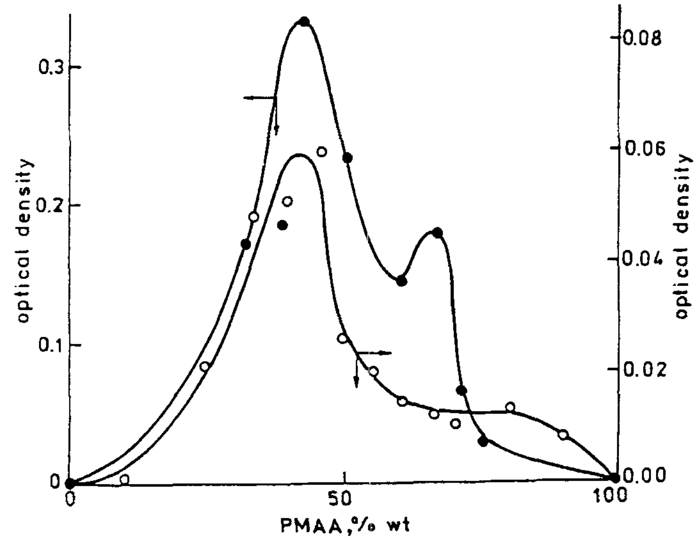

Figure 3. Turbidimetric curves for the aqueous solutions of PMAA-PNAI mixtures as a function of composition ($M_{n\,PNAI} = 7800$, $M_{v\,PMAA} = 150000$): (●) $c = 0.1$ g·dl^{-1}; (o) $c = 0.2$ g·dl^{1}.

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long PMAA chains to the PNAI short chains. The increase in η_{red} is more evident for the PNAI chains with low polymerization degrees.

The shape of the plots showed the formation of at least three different complexes, with a PMAA/PNAI molar composition of 2:3, 1:1, and 2:1, respectively. One or another prevails mainly as a function of oligomer dimensions. This must be considered as an effect of the known increase of the stability of the complexes with the increase in the chain length of any partner (i.e., an exponential dependence of the equilibrium constant with the polymerization degree) [16, 17]. The stability is determined by the shortest chain component. Thus, it appears from Figure 2 that with the increase of the PNAI length, the equilibrium gradually shifts to the preferential formation of the PMAA-PNAI complex with a 2:1 composition, which seems to be the most stable.

Turbidimetry

Solution concentration represents another influence factor. The turbidmetric study of the mixtures of the PMAA and PNAI solutions revealed that with increasing solution concentration the complex with a 2:1 PMAA/PNAI molar ratio becomes more important (Figure 3).

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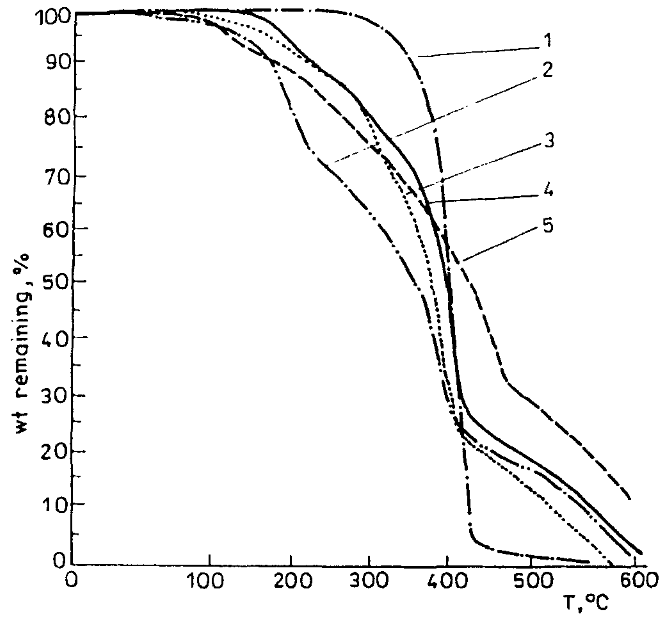

Figure 4. Typical thermograms for:
1 - homopolymer
2 - PMAA-PNAI blend (sample M_5)
3 - PMAA-PNAI synthetic complex (sample P)
4 - PMAA-PNAI template complex (sample TP_2)
5 - PMAA-PNAI template complex (sample T_2)
Heating rate: 12°C/min. For sample numbering, see Table 1.

Solid state properties

Thermal properties. TGA

Usually, complexation leads to more stable polymeric materials. For the PMAA-PNAI system a comparative image is presented in Figure 4, which shows thermogravimetric analysis (TGA) traces for the PNAI homopolymer and for the synthetic and template complexes.

It can be observed that the decomposition temperature for the interpolymer complex is higher as compared to that of the mixture of the two polymers. The stability increases in the order:

blend << synthetic complex ≤ template complex

PNAI oligomers are stable until 280°C minimum, when the scission of the acetyl groups begins, with the maximum weight loss at 400°C (Figure 4). PMAA

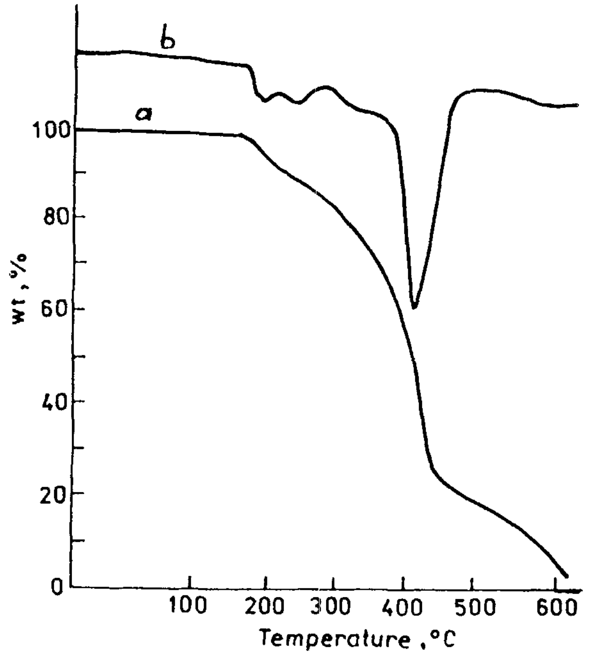

Figure 5. Thermogravimetric behavior of the sample TP_2
a) weight loss curve
b) first derivative curve; heating rate: 12°C/min.

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is known to have two decomposition regions [18]. The first stage, ascribed to an anhydration reaction between pairs of carboxyl groups of the structural units, starts at about 140°C and stops at cca. 260°C, with a maximum decomposition rate at 220°C. The second decomposition region, corresponding to the thermal degradation of the previously formed poly(methacrylic anhydride), begins at 300 °C and shows a maximum decomposition rate at 410°C. In the thermograms of the PMAA-PNAI blends and of the interpolymer complex, all mentioned decomposition regions are present in a lower or higher extent depending on composition and preparative method. A new region between cca. 130-190°C (weight loss of about 5%) with a maximum at 180°C appears; this one is visible especially in the complexes with a lower PMAA content (i. e., PMAA/PNAI ≈ 2/3), or in those synthesized by a template polymerization approach (Figure 5).

This supplementary weight loss was ascribed to a transamidation reaction occurring between the COOH groups of PMAA and the acetyl groups from PNAI,

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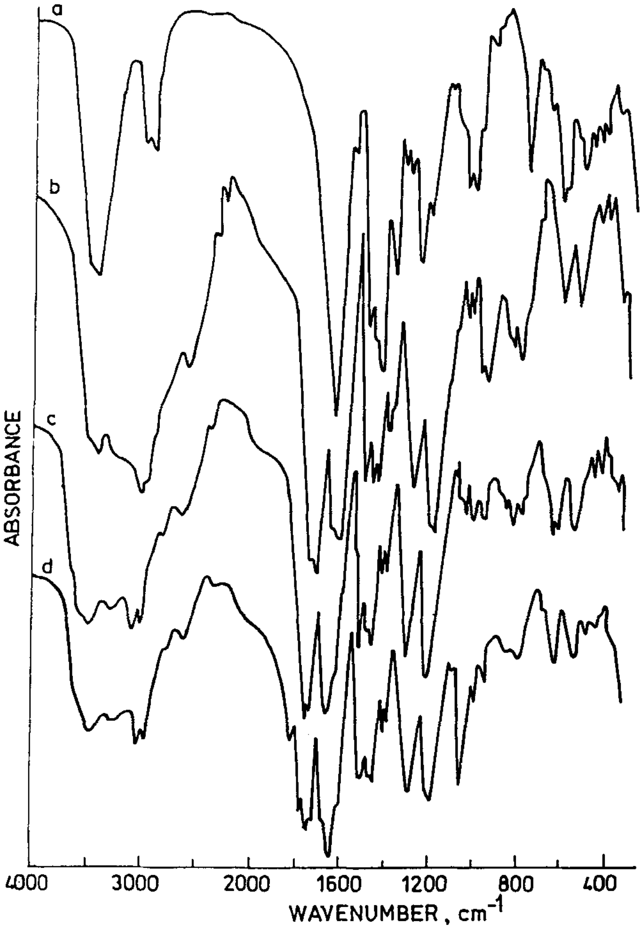

Figure 6. IR spectra for : a) PNAI homopolymer; b) sample T_2; c) sample P; d) sample P after 5 min. annealing at 190°C.

reaction favored by the mutual orientation of the side groups in the complex sequences.

The comparison of the IR spectra of sample P (Table 1) before and after a thermal treatment for 15 min. at 190°C sustains this supposition (Figure 6).

Thus, anhydride formation is obvious from the appearance (after annealing) of the characteristic absorptions at 1020 cm^{-1} (υ-C-O-C-), respectively at 1770 cm^{-1} and 1810 cm^{-1} (sim and asim stretching vibrations of C=O groups in anhydride ring). These results show that the anhydride structure is the six

Figure 7. FTIR spectrum (detail) of sample T_2 after annealing 30 min. at 150 °C.

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membered glutaric anhydride type ring [18], corresponding to the reaction between adjacent carboxyl groups. Accordingly, most of them are located in loops [4]. The total intensity of the absorbtion band attributed to C=O from COOH groups is decreased. In all complexes, this band is split. The new peak at 1738 cm^{-1}, which is assigned to the C=O groups involved in hydrogen bonding formed by complexation of PMAA with PNAI, is superposed with the peaks corresponding to C=O groups (free and dimerized) from the remaining PMAA chains.

The signal of the C=O group from the tertiary amide group is also split after sample annealing. The band at 1630 cm^{-1} overlapps with a new one at 1660 cm^{-1}. This band is also split in the complexes synthesized through a thermal treatment (i. e. samples of T type). The second peak is absent in the spectra of the synthetic complexes or template complexes obtained by photochemical polymerization (samples of TP type). The new signal was attributed to C=O from the amide groups formed after transamidation. The FTIR spectrum (Perkin Elmer apparatus) of the domain of interest evidences better the mentioned aspects (Figure 7).

The transamidation reaction might be used in the obtention of polymeric network structures or gels. Electro-erodible hydrogels were synthesized by polymer chain complexation of poly(N-propionyl iminoethylene) with poly(methacrylic acid) [19].

DSC measurements

DSC is an appropriate method used to distinguish the differences between various complexes [9, 16]. Typical DSC traces for the PMAA-PNAI system are shown in Figure 8.

The first run, from 20°C to 130°C, was performed to remove the water retained in the samples (weight loss 4-7 %). In the second run, from 20°C to 250°C, the DSC curve presents a T_g and an endotherm peak, located at 210-240°C, or two endotherm peaks (160-190°C - T_{max1} and 210-230 °C - $T_{max\,2}$). For the latter case, the Tg values were registered after a third scan.

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The location of the endothermic peaks is influenced by matrix dimension, complex composition, (see Table 2) and preparative procedure. The first endothermic peak, evident chiefly in the complexes synthesized by polymerization initiated by thermolysis of the PNAI macroinitiators, might appear as an effect of the transamidation reaction, which replaces the weak interchain bonds by stable covalent ones. The transamidation is most likely favored by the previous formation, during the polymerization process, of a few interchain amide bonds with a random distribution. This behavior is close to the accelerating effect of neighboring units in macromolecular reactions. A better orientation of COOH groups in the templates with short PNAI chains also facilitates the transamidation reaction. A similar transformation of the interchain noncovalent bonds into covalent ones was reported for poly(ethylenimine) - poly(methacrylic acid) complexes [4] or in polyacrylamide-poly(methacrylic acid) polycomplexes [17]. The second peak was ascribed to the intramolecular anhydration reaction of the carboxylic groups of the polyacid.

Figure 9 shows the glass transition temperatures as a function of blend or complex composition.

The transition temperatures for the blend fall below the weight-average line, this indicating relative weak specific intermolecular interactions.Dimethylformamide - the solvent used in the preparation of these samples - can be considered as a low molecular model for PNAI. Its presence implies a hindering of the complexation process between the two macromolecular partners.

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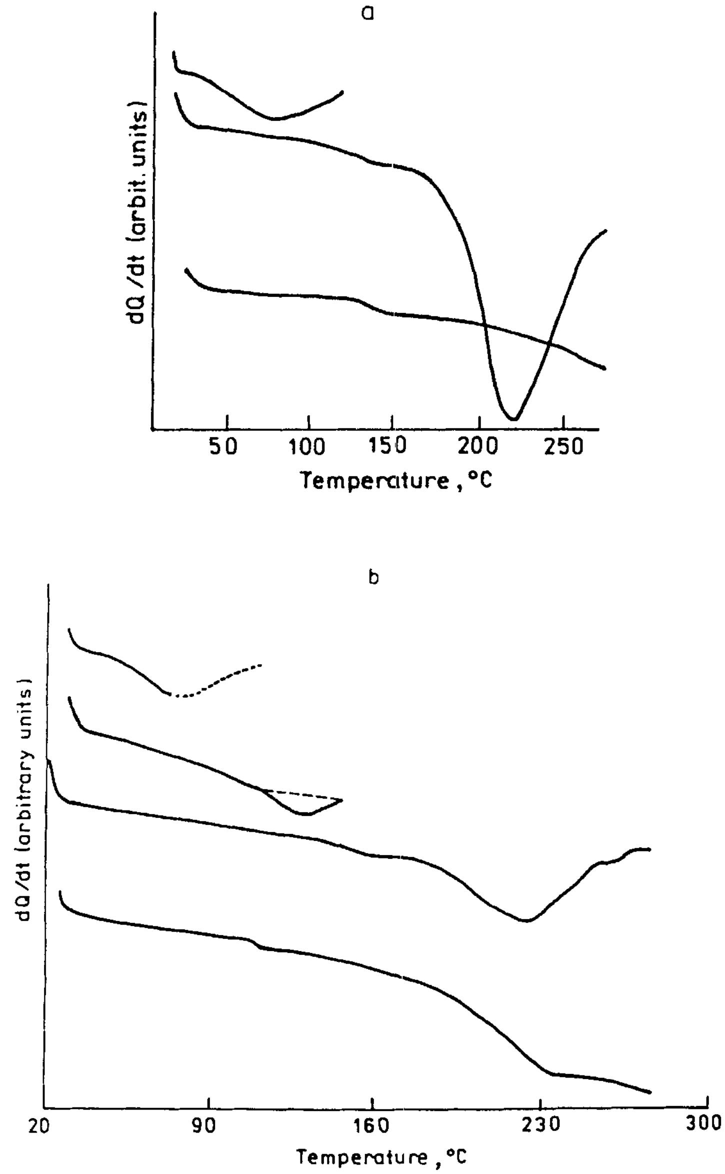

Figure 8. Typical DSC curves
a: sample P; b: sample T_7
Scan speed: 10°C/min.

TABLE 2. Thermal Characteristics of PMAA-PNAI Complexes as a Function of Template Length.

Sample code	Sequence DP_{PNAI}	PMAA/PNAI in copolymer	Third run			Fourth run	
			T_g	T_{max1}	T_{max2}	T_g	T_{max2}
T_4	21	0.7	43,180		235	45	243
T_5	21	1.5	-	108	232	136	
T_6	40	2.6	115	174	225	120, 204	
T_7	58	1.5	-	162	222	112, 209	
T_8	75	1.7	-	106	216	94, 200	

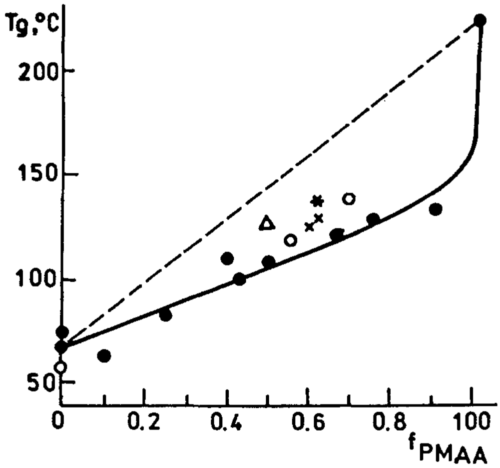

Figure 9. Glass transition temperatures of PMAA-PNAI blends and complexes (•) blends; (o) template complex (TP_1, TP_2); (x) synthetic complex (P); (∗) annealed synthetic complex (15 min. at 190°C, second run); Δ template complex (sample T_2).

In order to describe the Tg behavior of the blends, the modified Gordon-Taylor equation proposed by Uematsu and Honda [20]

$$Tg = w_1Tg_1 + kw_2Tg_2 + qw_1w_2/(w_1 + w_2)$$

where k is an adjustable parameter and q represents the contribution due to intermolecular interaction, has been used. The experimental curve was best fitted for values of 0.01 and 78.7 for k and q, respectively. However, other values might be

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considered as well. For poly(N-propionyliminoethylene)-poly(acrylic acid) system (blends cast from DMSO, a hydrogen bond breaking solvent) values of k = 0.1 and q = - [10] were reported [9].

As expected, the Tg values for the mutual precipitate and template complexes are higher than those of the corresponding blends, suggesting a stronger packing. This effect increased with the lowering of the polymerization degrees of the partners implied in the complexation process (Table 2), as a consequence of higher order in the chain packing [14]. These results are in agreement with literature data [9, 16].

The Tg values of the template complexes obtained by different approaches are very close for a similar dimension of the PNAI template chain and increase following sample annealing. The last aspect may be related to the orientation degree increase of COOH groups by annealing and also to a higher probability of occurrence of the two discussed side reactions.

The partial transformation of the complexes by transamidation coupled with the intramolecular anhydration of the COOH groups leads to a segregated structure, the products acting as block copolymers comprising sequences with different structures and properties (see Table 2, fourth run). The first Tg was ascribed to the complexed sequence and the second one was attributed to the sequence modified by anhydration.

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X-ray diffraction analysis

According to the results, template polymerization was expected to lead to better ordered complexes, as compared to the synthetic ones and/or to the blends. However, WAXS patterns of the PMAA - PNAI template complex, synthetic complex and blend present only broad bands of similar shape. Even if the qualitative interpretation is in agreement with other experimental observations, no quantitative data could be obtained.

CONCLUSIONS

PNAI-PMAA pairs have the ability to interact by hydrogen bonding involving the C=O from the tertiary amide and the COOH groups from the polyacid.

The viscometric and turbidimetric measurements evidenced the formation of more than one complex. Their composition is a function of solvent nature, partners length, preparative technique, feed composition, and solution concentration.

The hydrogen bonding interaction is negligible in films cast from DMF (blends). The higher degree of orientation of the interacting groups as a consequence of complex formation yields an increased density of packing and thus higher Tg values for the polymeric systems obtained by mutul precipitation from aqueous solutions or by template polymerization.

The TGA, DSC and IR data establish the physical bond replacement in the intermolecular complexes.

The specific solution and solid state behavior of the PNAI-PMAA system is the result of the associative ability of both partners (PNAI is a highly ordered, crystallizable polymer, while PMAA affords the forming of physical dimeric structures through the association of neighboring COOH groups).

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REFERENCES

[1] M. M. Coleman, J. F. Graz , and P. C. Painter, *Specific Interactions and Miscibility of Polymer Blends*, Technomic Publishing Co., Lancaster, Pennsylvania 1991.

[2] S. Lu, E. M. Pearce, and T. K. Kwei, *J. Macromol. Sci. - Pure Appl. Chem.*,*A31*, 1535 (1994).

[3] a) H. A. Schneider, H. J. Cantow, and V. Percec, *Polym. Bull.*, *6*, 617 (1982).

b) U. Epple and H. A. Schneider, *Thermochim Acta*, *160*, 103 (1990).

[4] N. A. Plate, A. D. Litmanovich, and O. V. Noah, *Macromolecular Reactions. Peculiarities, Theory and Experimental Approaches*, J. Wiley & Sons, Chichester, 1995, Chap. 7.

[5] Y. Osada and Y. Takeguchi, *Polym. J.*, *15*, 279 (1983).

[6] S. E. Kudaibergenov, Z. S. Nurkeeva, G. A. Mun, B. B. Enmukhamketova , and A. T. Akbanova, *Macromol. Chem. Phys.*, *196*, 2203 (1995).

[7] S. S. Al-Alawi, *Macromolecules*, *24*, 4206 (1991).

[8] A. Frank, *Makromol. Chem.*, *96*, 258 (1966).

[9] P. Lin, C. Clash, E. M. Pearce, and T. K. Kwei, *J. Polym. Sci.: Part B: Polym. Phys.*, *26*, 603 (1988).

[10] S. Shenkov and V. Yu. Baranovsky, *J. Polym. Sci.: Part A: Polym. Chem.*, *32*, 1385 (1994).

[11] a) S. Kobayashi, H. Uyama , and Y. Narita, *Macromolecules*, *23*, 353 (1990).

b) S. Kobayashi, H. Uyama, Y. Narita , and Y. Ishiyama, *Macromolecules, 25*, 323 (1992).

[12] N. N. Wiederhorn and A. M. Brown, *J. Polym. Sci., 8*, 651 (1952).

[13] C. I. Simionescu, G. David, A. Ioanid, V. Paraschiv, G. Riess , and B. C. Simionescu, *J. Polym. Sci.: Part A: Polym. Chem., 32*, 3123 (1994).

[14] C. I. Simionescu, G. David, V. Paraschiv, A. Ioanid, S. Manolache, and B. C. Simionescu, *J. Polym. Sci.: Part A: Polym. Chem., 34*, 3071 (1996); C. I. Simionescu, V. Paraschiv, G. David, and B. C. Simionescu, *Eur. Polym. J.*, in press.

[15] G. David, V. Bulacovschi, O. Ciochina , and B. C. Simionescu, *J. Macromol. Sci.- Pure & Appl. Chem., A32*, 8 /9, 1649 (1995).

[16] a) H. T. van de Grampel, Y. Y. Tan , and G. Challa, *Macromolecules, 25*, 1049 (1992).

b) H. T. van de Grampel, Y. Y. Tan , and G. Challa, *Macromolecules, 25*, 1041 (1992).

[17] V. Yu. Baranovsky, L. A. Kazarin, A. A. Litmanovich , and I. M. Papisov, *Eur. Polym. J., 20*, 191 (1984).

[18] B. C. Ho, Y-Der Lee , and W. K. Chin, *J. Polym. Sci.: Part A: Polym. Chem., 30*, 2389 (1992).

[19] Y. H. Bae, I. C. Kwon, C. M. Pai , and S. W. Kim, *Macromol. Chem. Macromol. Symp.* 70/71, 173 (1993).

[20] I. Uematsu and K. Honda, *Rep. Progr. Polym. Phys. Japan, 8*, 111 (1965).

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