DEODATO RADIĆ*), NICOLÁS GATICA,
LIGIA GARGALLO

Departamento de Química Física, Faculted de Química
Pontificia Universidad Católica de Chile
Casilla 306, Correo 22, Santiago, Chile
e-mail: dradic@puc.cl

Blends of poly(hydroxypropyl methacrylate) with 4-vinyl-*co*-*N*-vinyl-2-pyrrolidone and with vinyltrimethylsilane-*co*-*N*-vinyl-2-pyrrolidone copolymers. The effect of copolymer composition on interpolymer compatibility

Summary — Glass transition temperatures (Figs. 1, 3), DSC and TGA thermograms (Figs. 2, 4), and Fourier transform infrared (FTIR) spectra (Fig. 5) showed the binary blends (Table 1) of poly(2-hydroxypropyl methacrylate) (PHPMA) with 4-vinylpyridine-*co*-*N*-vinyl-2-pyrrolidone (4-VPy-*co*-VP) to be compatible over the whole range of compositions. The blends of PHPMA with vinyltrimethylsilane-*co*-*N*-vinyl-2-pyrrolidone (VTMS-*co*-VP) were found to be compatible up to VTMS contents of ~ 25 wt. %. The former blends (Figs. 1, 2) are believed to be compatible on account of H-bonding of PHPMA's OH with the 4VPy and VP units of 4VPy-*co*-VP. In the latter blends, up to 25.7% of VTMS, H-bonds between PHPMA's OH groups and VP units suffice to provide compatibility, but at >25.7 wt. % VTMS, hydrophobic interactions of the VTMS moieties prevail and phase separation occurs.

Key words: polymer—copolymer blends, interpolymer compatibility, phase separation, poly(2-hydroxypropyl methacrylate), 4-vinylpyridine-*co*-*N*-vinyl-2-pyrrolidone and vinyltrimethylsilane-*co*-*N*-vinyl-2-pyrrolidone copolymers.

Mixing of two materials to get a balance of properties hardly available in any of them individually has been successfully exploited, *e.g.*, by chemical combination of different monomers to yield random, block or graft copolymers and by chemical modification of classical polymers. At present, this subject is important in the academic and industrial research dealing with this kind of materials [1].

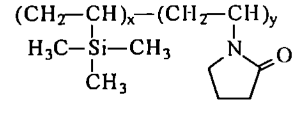
Most hydrocarbon polymers do not mix, *i.e.*, they form parts of inmiscible polymer blends. This is a consequence of a negligibly low combinatorial entropy and of a positive enthalpy term, because the only intermolecular forces acting in the system are London dispersion or van der Waals forces. In order to obtain compatible polymer blends, attractive forces are required to occur between dissimilar and potentially interacting segments [2]. Thus, it is possible to promote different kind of interactions like dipole-dipole, acid-base, charge transference, *etc*. These interactions can be promoted by the structurally dissimilar units incorporated in the polymer functionalization process. Homopolymerization (or copolymerization) of functionalized monomers [3—6] or modification of previously synthesized polymers [7] are two ways to obtain functionalized polymers or copolymers.

The study on the compatibilization of copolymeric materials is, therefore, of special interest. In this kind of materials, the monomer units differing in chemical nature, should influence directly the polymer miscibility. Copolymers containing vinylsilicon moieties [8] and *N*-vinyl-2-pyrrolidone (VP) along with aromatic comonomers have been previously reported [9]. The effect of the comonomer structure and the composition seems to play an important role in the thermodynamic and conformational behavior of these kinds of macromolecules. The combination of *N*-vinyl-2-pyrrolidone with aromatic comonomers like 2-vinylpyridine (2VPy) or 4-vinylpyridine (4VPy) and vinyltrimethylsilane (VTMS) through a copolymerization process is a way to obtain

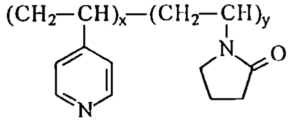
---

*) To whom all correspondence should be addressed.

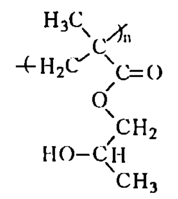
amphiphilic copolymers. Such copolymers should be able to interact with polar and non polar systems depending on the composition.


(I)

VTMS-*co*-VP


(II)

4VPy-*co*-VP


(III)

PHPMA

The aim of this work is to study the effect of copolymer composition on the blending process of functionalized copolymers. In order to reach this objective, copolymers of 4VPy with VP (4VPy-*co*-VP) and of VTMS with VP (VTMS-*co*-VP) previously synthesized and characterized [3, 4] were blended with poly(2-hydroxypropyl methacrylate) (PHPMA). The effect of the specific interactions on miscibility was studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR).

EXPERIMENTAL

Preparation of monomers and polymers

Aldrich's PHPMA, weight-average molecular weight $\overline{M}_w$ = 30 000, was used. Copolymers 4VPy-*co*-VP and VTMS-*co*-VP were obtained in the bulk at 323 K by using 2,2'-azobisisobutyronitrile (AIBN) as previously reported [3, 4]. The copolymers were characterized by ^{1}H-NMR and FTIR spectra [3, 4]. Copolymer composition was determined by elemental analysis of VTMS-*co*-VP and by UV-VIS spectroscopy of 4VPy-*co*-VP.

TGA measurements

Dynamic thermogravimetric measurements were performed by using a Mettler TA-3000 calorimetric system, equipped with a TC-10A processor and a TG-50 thermobalance with a Mettler MT5 microbalance. Samples were heated in Al_2O_3 pans. Measurements were carried out between 308 and 1073 K at 20° · min^{-1} under N_2. The thermogravimetric data were processed by the Mettler 821 calorimetric system using the STAR© program.

Preparation of blends

Blends of different compositions were prepared by solution casting using ethanol as solvent and then evaporated at room temperature and vacuum dried at 298 K for 120 h. The polymer concentration in the solution was about 2% w/w.

DSC measurements

The glass transition temperatures (T_g) of the pure polymers, copolymers and blends were measured with a Mettler TA-3000 system equipped with a TC-10A processor with a DSC-20 cell. Polymer samples were dried under reduced pressure in a vacuum oven prior to the measurements. Dry nitrogen was used as a purge gas and thermograms were measured within the range 308 to 523 K at a scan rate of 20° · min^{-1}.

FTIR spectra

Infrared spectra of pure polymers and blends were recorded on a Vector 22 Bruker Fourier transform infrared spectrophotometer. Spectra were recorded with a resolution of 1 cm^{-1}. Samples were prepared directly in KBr pellets.

RESULTS AND DISCUSSION

Table 1 lists the compositions of 4VPy-*co*-VP and VTMS-*co*-VP copolymers [3, 4]. The T_g values of the copolymers at different compositions and the intrinsic viscosities [η] in ethyl alcohol as an approximate estimation of the molecular weights of the samples are also summarized in Table 1.

Table 1. Copolymer compositions, glass transition temperatures (T_g) and intrinsic viscosity in ethyl alcohol for 4VPy-*co*-VP and VTMS-*co*-VP

Copolymer	Copolymer composition 4VPy, mol %	T_g, °C	[η], dL · g^{-1}
I	38.8	177.9	0.17
II	69.6		0.26
III	73.2	150.2	0.40
IV	84.5		0.40
V	92.6	153.7	0.45
	VTMS, mol %		
VI	19.3	166.9	0.94
VII	23.3	165.8	0.50
VIII	25.7	165.6	0.36
IX	28.2	161.5	0.33
X	34.7	153.6	0.21

The DSC thermograms of dried blends of PHPMA with 4VPy-*co*-VP of various compositions (I, III and V, Table 1), exhibited distinct single glass transition temperatures (T_g), indicative of a one-phase material. It is well known that a single T_g value for a binary polymer blend reflects miscibility and the blend can be considered to be a single-phase material [10—12]. In Fig. 1, the T_g-data are presented in relation to the composition of the blend. The T_g-values of the blends are intermediate between those of the pure components. They are lower than those of the corresponding 4VPy-*co*-VP copolymer but higher than that of pure PHPMA. This result indicates the miscibility over the whole range of compositions, irrespective of the 4VPy-*co*-VP composition. This behavior can be attributed to the presence of hydrogen bonding interactions. The hydroxyl group of PHPMA is able to interact with both the 4VPy and the VP units of 4VPy-*co*-VP, and these interactions responsible for the occurrence of only one T_g-value.

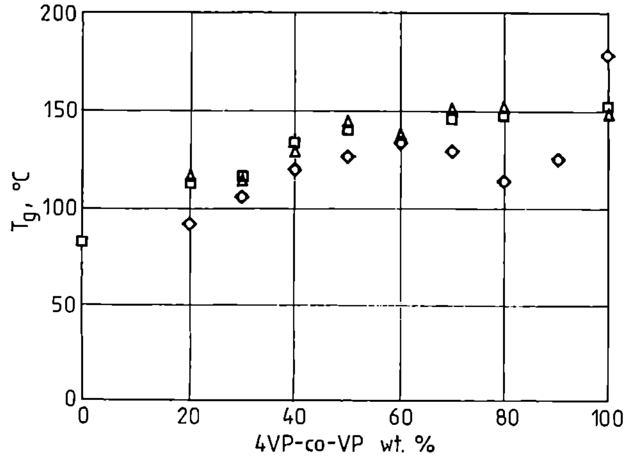


Fig. 1. Glass transition temperatures T_g for blends containing PHPMA and 4VPy-co-VP (I) (◇), 4VPy-co-VP (III) (□) and 4VPy-co-VP (V) (△) in relation to blend composition

Figure 2a shows the representative thermogravimetric profiles for a (50:50 w/w) blend of 4VPy-*co*-VP with PHPMA and for the corresponding pure components. Intermediate thermogravimetric profiles of the blends between those of the corresponding pure components have been reported as evidence for polymer—polymer miscibility [13]. Figure 2b presents the first derivative of weight loss (dm/dT) with respect to temperature. This allows to observe the position of the maximum more conveniently. The thermogravimetric data can be considered to be another evidence indicating miscibility.

Figure 3 shows the variation of T_g with blend composition in the VTMS-*co*-VP/PHPMA system. In this case, the copolymer composition is seen to affect the compatibility. Up to 25.7 mol % of VTMS (VI and VIII, Table 1), no phase separation is observed (squares and rhombs in Fig. 3). The VP present in the copolymer is seen to promote the interpolymer miscibility *via* possible specific interactions such as hydrogen bonding between the hydroxyl group of PHPMA and VP. At higher VTMS contents (X, Table 1), phase separation takes place (triangles in Fig. 3) in the blends containing up to 50% of VTMS-*co*-VP. One phase system results when the VP

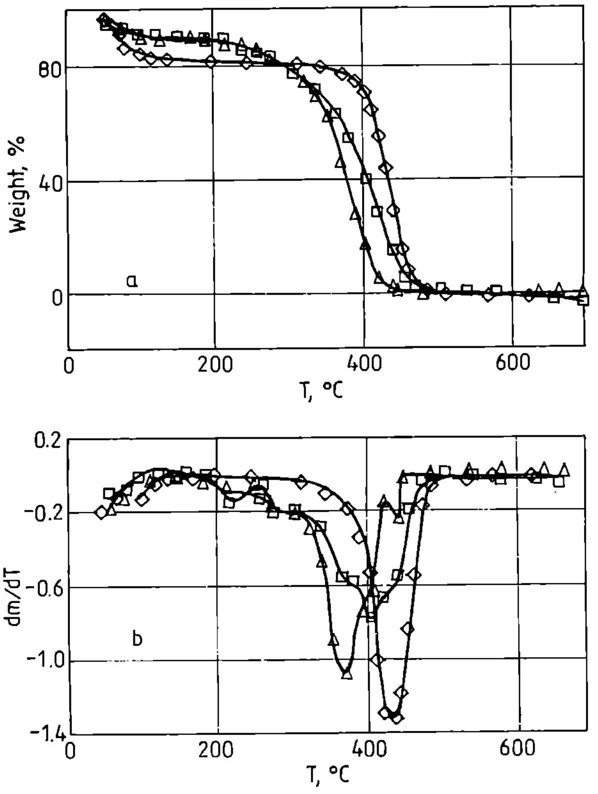


Fig. 2. Thermogravimetric profiles and (b) the first derivative of weight loss dm/dT with respect to temperature for (50:50 w/w) 4VPy-co-VP (III)/PHPMA blend and for pure components: III 100% (◇), III/PHPMA 50/50% (□), PHPMA 100% (△)

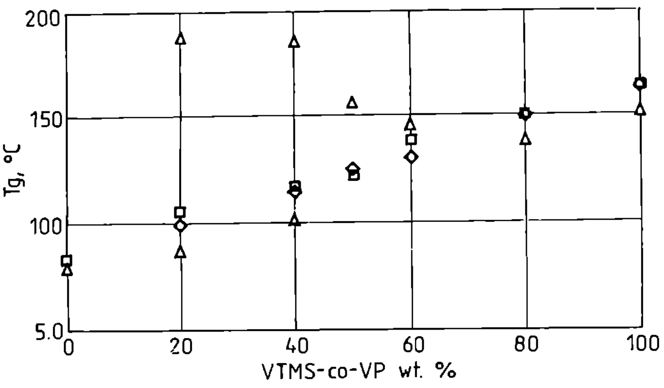


Fig. 3. Glass transition temperatures T_g for blends containing PHPMA and (a) VTMS-co-VP (VI) (◇), (b) VTMS-co-VP (VIII) (□) and (c) VTMS-co-VP (X) (△)

content in the copolymer is increased, presumably on account of interactions of VP units with PHPMA.

The DSC results obtained for the VTMS-*co*-VP /PHPMA blends are confirmed by TGA measurements. Figures 4a, b show the thermogravimetric profiles of the blends and the corresponding pure components. In the first case, a (50:50 w/w) VTMS-*co*-VP (VI)/PHPMA blend shows only one T_g (squares and rhombus in Fig. 3) and presents a behavior similar to that of compatible polymer blends of 4VPy-*co*-VP/PHPMA (Fig. 2a). In the second case, a (40:60 w/w) VTMS-*co*-VP (X)/PHPMA blend, with one or two T_g depending on the blend composition (triangles in Fig. 3), exhibits no clear intermediate thermogravimetric profile between the corresponding pure components.

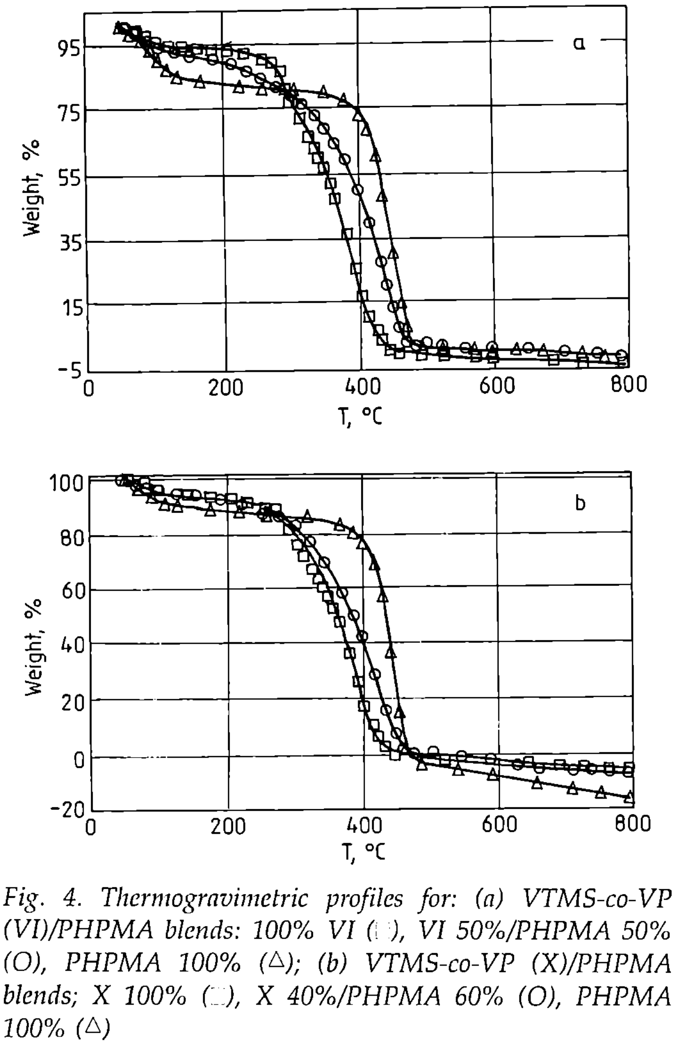


Fig. 4. Thermogravimetric profiles for: (a) VTMS-co-VP (VI)/PHPMA blends: 100% VI (□), VI 50%/PHPMA 50% (O), PHPMA 100% (△); (b) VTMS-co-VP (X)/PHPMA blends; X 100% (□), X 40%/PHPMA 60% (O), PHPMA 100% (△)

IR spectroscopy can be used to detect and identify the molecular interactions both in pure polymers, by association of similar molecules, and in blends due to the association of different species [1, 13—17]. The variation of the band corresponding to a chemical group toward lower frequencies and an increase in its width are considered to be the evidence for specific interactions [1]. FTIR spectra of the VTMS-*co*-VP/PHPMA blends allow to distinguish the carbonyl groups of VP and PHPMA. By this way it is possible to follow the variation of one carbonyl group or both. Figure 5 shows the wavenumber corresponding to >C=O group in the copolymer VTMS-*co*-VP in the blends with PHPMA in relation to composition. For the VTMS-*co*-VP (VI)/PHPMA and VTMS-*co*-VP (VIII)/PHPMA blends, which produce only one T_g over the whole range of blend compositions, the wavenumber is seen to decrease. This result indicates to interactions like hydrogen bonding formation take place between the polymers and therefore compatibility occurs. The VTMS-*co*-VP (X)/PHPMA blend, shows as variation in the >C=O wavenumber. This VTMS-*co*-VP contains the highest content of the VTMS units (~ 35 mol %), which are not able to interact with the PHPMA chains carrying carbonyl groups. For this reason, the band corresponding to carbonyl stretching remains almost unchanged.

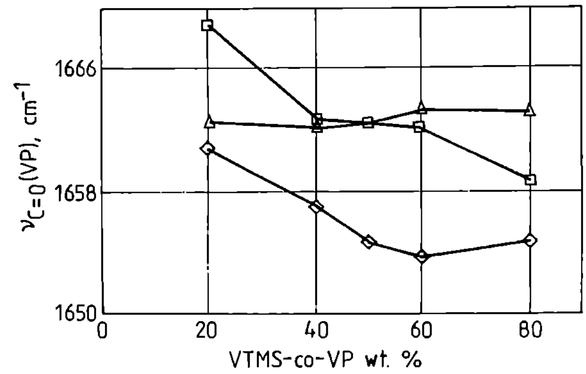


Fig. 5. Wavenumber corresponding to >C=O group of the copolymer in the blends of PHPMA with: VTMS-co-VP [VI] (◇), VTMS-co-VP [VIII] (□), VTMS-co-VP [X] (△) in relation to blend composition

CONCLUSIONS

Miscibility within the whole range of compositions is observed in 4VPy-*co*-VP/PHPMA blends considering the existence of single glass transition temperature. In this case, the presence of specific interactions like hydrogen bonding between the copolymer, like acceptor polymer, and PHPMA, like donor polymer should be the responsible for this behavior. 4VPy-*co*-VP has two kinds of monomer units able to interact with PHPMA. For this reason, no phase separation is observed, irrespective of blend composition.

In VTMS-*co*-VP, the presence of hydrophobic VTMS units gives rise to phase separation in the VTMS-*co*-VP/PHPMA blend at low copolymer contents above a certain critical value of copolymer composition.

ACKNOWLEDGMENT

We express our thanks to FONDECYT, Grant 8970011, for partial financial support. N. G. thanks to CONICYT for Doctoral Fellowship and to FONDECYT Projects 2960022 and 4990018 for partial financial support.

REFERENCES

1. Rocha M.: *Rev. Plast. Mod.* 1993, **440**, 149.
2. Urzúa M., Opazo A., Gargallo L., Radić D.: *Polym. Bull.* 1998, **40**, 63.
3. Gatica N., Gargallo L., Radić D.: *Polym. Int.* 1998, **45**, 285.
4. Gatica N., Díaz F. R., Gargallo L., Radić D.: *Polym. Bull.* 1998, **40**, 707.
5. Gan L. H., Roshan Deen G., Gan Y. Y.: *Eur. Polym. J.* 1998, **34**, 33.
6. Demirelli K., Coskun M., Erol I.: *Eur. Polym. J.* 1999, **36**, 83.
7. Reinecke H., Mijangos C.: *Macromol. Chem. Phys.* 1998, **199**, 2199.
8. Bajaj P., Gupta D. C., Babu G. N.: *J. Macromol. Sci.* 1983, **A20**, 527.
9. Huglin M. B., Khairou K. S.: *Eur. Polym. J.* 1988, **24**, 239.
10. Olabisi O., Robeson L. M., Shaw M. T.: "Polymer—polymer miscibility", Academic Press, New York 1979.
11. Paul D. R., Newman S.: "Polymer Blends", Academic Press, New York 1978.
12. Luo X., Goh S. H., Lee S. Y.: *Macromolecules* 1997, **30**, 4934.
13. Meaurio E., Velada J. L., Cesteros L., Katime I.: *Macromolecules* 1996, **29**, 4598.
14. High M. S., Painter P. C., Coleman M. M.: *Macromolecules* 1992, **25**, 797.
15. Gargallo L., Gatica N., Radić D.: *Intern. J. Polymeric Mater.* 1994, **27**, 107.
16. Liu Y., Goh S. H., Lee S. Y., Huan C. H. A.: *Macromolecules* 1999, **32**, 1967.
17. Goh S. H., Liu Y., Lee S. Y., Huan C. H. A.: *Macromolecules* 1999, **32**, 8595.

KALENDARZ IMPREZ

cd. ze str. 802

4—8 listopada 2002 r. Taipei, Tajwan. **„Polymer Processing Society — Asia/Australia Meeting PPS-2002".**

Organizatorzy: Chang Gung University + The Polymer Processing Society, Taipei.

Tematyka ogólna: formowanie wtryskowe, wytłaczanie, reologia mieszaniny i stopy polimerowe, prace związane z rozwojem zagadnień morfologii i struktury polimerów, kształtowanie termiczne, formowanie z rozdmuchiwaniem, formowanie obrotowe, modelowanie matematyczne, przetwarzanie reaktywne, kompozyty polimerowe, włókna i folie, sporządzanie mieszanek gumowych i mieszanin polimerowych, właściwości mechaniczne, optyczne i elektryczne.

Tematyka specjalistyczna: przetwarzanie żywności, uwidocznianie przepływu, czujniki w procesie przetwarzania, formowanie wtryskowe wspomagane gazem, biopolimery, zastosowania w optyce i elektronice/elektrotechnice, nowe procesy przetwórcze.

Informacje: Dr Shih-Jung Liu, PPS Meeting 2002, Polymer Rheology and Processing Lab, Mechanical Eng., tel.: 886-3-3288 566, fax: 886-3-3972 558, e-mail: shihjung@mail.cgu.edu.tw lub pps2002@mail.cgu.edu.tw; http://pps.cgu.edu.tw.

9—13 listopada 2002 r. Makuhari, Japonia. Największe w Azji targi „Plastic and Rubber Trade Show".

Organizator: International Plastic Fair (IPF).

Informacje: IPF, Show Management Office, Kasumigaseki Bldg. 12F, 3-2-5 Kasumigaseki, Chiyoda-Ku, Tokio 100-6012, Japan. Tel.: +81-3-3503-7320, fax: +81-3-3503-7620, internet: http://www.a-tex.co.jp/plasttics.

2—5 grudnia 2002 r. Kyoto, Japonia. **IUPAC Polymer Conference on the Mission and Challanges of Polymer Science and Technology** (IUPAC-PC 2002).

Organizatorzy: IUPAC Macromolecular Division + Science Council of Japan (SCJ) + The Society of Polymer Science, Japan (SPSJ).

Informacje: IUPAC-PC 2002 Secretariat, The Society of Polymer Science, Shintomicho-Tokyu Building, 3-10-9 Irifune, Chuo-ku, Tokyo.