Thermal behaviour of poly(methacrylic acid)/poly(\(N\)-vinyl-2-pyrrolidone) complexes

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Received 18 December 1999; received in revised form 17 January 2000; accepted 29 February 2000

Abstract

Poly(methacrylic acid)/poly(\(N\)-vinyl-2-pyrrolidone) (PMAA/PVP) complexes were prepared by two different procedures: simple mixing of preformed PMAA and PVP and radical polymerization of methacrylic acid in aqueous solution in the presence of poly(\(N\)-vinyl-2-pyrrolidone) (template polymerization). Differential scanning calorimetry, thermogravimetric analysis and Fourier-transform infrared spectroscopy were performed to evaluate the properties of the two kinds of complexes and to establish if they showed chemico-physical differences that could be related to the preparation procedure. The results of our investigation indicated that the behaviour of these complexes is qualitatively similar, although it was observed that in the case of the complexes produced by blending, the process of PMAA anhydridization induced by a programmed thermal treatment of the samples, was less favoured. This suggests that by template polymerization it is possible to prepare PMAA/PVP complexes having a more ordered structure than that of similar complexes produced by simple mixing of the preformed components. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Template polymerization (TP) consists of the preparation of a polymer (daughter polymer) in the presence of a macromolecular compound (template or parent polymer) which can exert various effects on the polymerization [1–7]. It is assumed that the template induces an ordering effect on monomer molecules and a polycomplex is obtained as the reaction product.

The aim of this work is the preparation and characterization of poly(methacrylic acid)/poly(\(N\)-vinyl-2-pyrrolidone) (PMAA/PVP) complexes by both radical polymerization in aqueous solution of methacrylic acid (MAA) on PVP as a template and simple mixing (SM) of the two preformed polymers.

With regard to the PMAA/PVP polycomplexes produced by TP, it is known from the literature that PVP affects the radical polymerization of MAA performed not only in solvents (water, methanol, dimethylformamide) where both PVP and PMAA are soluble [8–10] but also in a solvent, such as benzene [8], where PMAA is insoluble. It was proposed that on reaching a critical length, the PMAA growing chains associate with the template by hydrogen bonding and then propagate in contact with the template forming a polycomplex (pick-up mechanism). By this way, a considerable acceleration of MAA polymerization rate, with respect to that of the polymerization performed in the absence of PVP (blank polymerization), is observed.

PMAA/PVP polycomplexes can also be prepared by mixing aqueous solutions of the two preformed macromolecules. However, in these conditions, the polymer chains are in the form of a random coil; therefore, not all the functional groups of one component are allowed to pair with those of the other component, and then, complexes with different properties with respect to those produced by TP are expected to be produced.

In this work, MAA was polymerized in aqueous solution in the presence of different amounts of PVP, and the polymerization kinetics was studied by dilatometry. Equimolar PMAA/PVP complexes obtained as reaction...
products were investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and Fourier-transform infrared (FTIR) spectroscopy in order to compare their properties with those of similar complexes obtained by SM.

2. Experimental

Methacrylic acid, poly(vinyl pyrrolidone) (MW = 55,000) and potassium persulphate (KPS 99.99% purity) were provided by Aldrich Chemie.

The monomer was purified by distillation under vacuum and stored at a low temperature.

2.1. Polymerization procedures

The MAA polymerizations were performed in degassed aqueous solutions using KPS (1 \times 10^{-2} \text{ M}) as radical initiator. Two initial monomer concentrations ([\text{MAA}]_{0} = 0.25 \text{ M and } [\text{MAA}]_{0} = 0.4 \text{ M}) were used. The initial template unit to monomer molar ratio (T/M) was varied between 0 and 1.0, varying the template concentration. The time–conversion curves were obtained dilatometrically using a 13.8 ml glass dilatometer. After filling the dilatometer with the reaction solution, a small volume of toluene was added in order to fill the capillary, then the dilatometer was put into a bath thermostated at 55 \pm 0.1 \text{\degree C} and the fall of the meniscus in the capillary was measured using a cathetometer.

2.2. SM complexes preparation

The SM polycomplexes were prepared by mixing 0.6 M aqueous solutions of commercial PVP and PMAA obtained by blank polymerization (T/M = 0).

2.3. Characterization

Stoichiometric polycomplexes obtained by both TP and SM were washed several times with distilled water and subsequently with methanol, dried under vacuum and powdered. In order to completely remove water, the samples were maintained at 105\degree C for 30 min under nitrogen flux before characterization by DSC, TGA and FTIR spectroscopy.

2.4. Differential scanning calorimetry

The thermal behaviour of pure PMAA, pure PVP and PMAA/PVP complexes was studied by a Mettler 25 DSC, using aluminum pans. Each sample was analyzed over a temperature range from 60\degree C to 500\degree C at a scan rate of 10\degree C/min.

2.5. Thermogravimetric analysis

The thermogravimetric analysis was carried out with a Mettler TG 50 thermobalance, under nitrogen flux over a temperature range from 35\degree C to 500\degree C at a scan rate of 10\degree C/min.

2.6. Fourier-transform infrared spectroscopy

FTIR spectra were measured on a Perkin–Elmer 1600 FTIR spectrophotometer. The samples in the form of powder were incorporated into pressed KBr (potassium bromide) plates. These plates were analyzed both before and after heating at 200\degree C for 1 h.

3. Results and discussion

The time–conversion curves for MAA polymerizations onto PVP at different T/M ratios (obtained by varying the template concentrations) can be seen in Figs. 1 and 2. In both the cases, it can be observed that all the polymerizations performed in the presence of the template show higher initial rates with respect to the blank polymerization. In addition, the initial polymerization rate increases as the T/M ratio increases. The value of the relative initial polymerization rate \(R_p/R_{pb}\) (initial polymerization rate in the presence of PVP/initial polymerization rate in the absence of PVP) was calculated for \(T/M = 0.945\), and it was found that \(R_p/R_{pb} = 6.8\) for \([M]_{0} = 0.25\) and \(R_p/R_{pb} = 3.9\) for \([M]_{0} = 0.4\). According to the literature [8–10], it is well evident that PVP affects the MAA polymerization kinetics inducing an increase in the polymerization rate in spite of the increase of the viscosity of the reaction medium due to the presence of...
the template and the polycomplex formed. Moreover, our results indicate that the \( R_p/R_m \) value increases by lowering the initial monomer concentration.

PMAA/PVP polycomplexes produced by both TP and SM were characterized by DSC, TGA and FTIR spectroscopy. In order to understand better the properties of these polycomplexes, the behaviour of PMAA and PVP homopolymers has to be taken into account first.

PMAA shows a good thermal stability until about 180°C, then in the 180–240°C temperature range, an endothermic peak corresponding to a first degradation process can be observed. Above 240°C, no relevant thermal events occur till 420°C, when a second endothermic event corresponding to the decomposition of the polymer starts. The PMAA thermogravimetric analysis trace and the corresponding first derivative curve show that both these endothermic events are associated with the weight loss of the sample.

As reported by McNeill et al. [11,12], the first degradation process is related mainly to the loss of water molecules through the formation of intra- and intermolecular anhydride links and also to the decarboxylation of a fraction of the –COOH groups by which CO2 is formed. In the second degradation stage, the polymer decomposes with the elimination of CO and CO2 by way of abundant backbone scission and formation of a small concentration of unsaturation.

With regard to PVP, it is stable over a wide range of temperature and starts to degrade at about 380°C. The DSC (Fig. 3) and TGA analyses results in that the PMAA/PVP polycomplexes behaviour corresponds to the superimposition of those of the two components. In fact, the DSC thermograms show two endothermic peaks: the first corresponding to the first degradation of PMAA and the second corresponding to the contemporory decomposition of PMAA and PVP. The TGA traces confirm this behaviour showing for both kinds of complexes, a first little weight loss ascribable to PMAA anhydridization and a second more pronounced weight loss related to the material degradation. It is interesting to note that in the case of SM complexes both DSC and TGA show that the first degradation process occurs at a temperature higher with respect to that of both the TP complexes and pure PMAA.

FTIR spectroscopy was carried out in order to verify whether the first polycomplex degradation event corresponds to PMAA anhydridization. Samples of equimolar (calculated per base mole units) TP and SM polycomplexes were analyzed before and after thermal treatment performed at 200°C for 1 h. Fig. 4 shows the FTIR spectra. Curve a, corresponding to a TP polycomplex before heating, shows two bands that indicate the interactions occurring between PMAA and PVP: a band \( \nu \text{CO} = 1722 \text{ cm}^{-1} \) for –COOH groups of PMAA bound by H-bonds with oxygen atoms of PVP and a band \( \nu \text{O=O} = 1650 \text{ cm}^{-1} \) which corresponds to the valence vibrations in the free carbonyl groups of PVP combined into the polycomplex with PMAA. Other bands of interest are characteristic of PMAA: a band at 3440 cm\(^{-1}\) corresponds to some water molecules associated with the –COOH groups and the other three bands at 1391, 1267 and 930–964 cm\(^{-1}\) are also due to the acid dimer.

In the FTIR spectrum of the same complex after heating (curve b), the formation of anhydride links as a consequence of the thermal treatment is clearly evidenced by the disappearance of the 1722 cm\(^{-1}\) band and by the appearance of three peaks at 1804, 1750 and 1020 cm\(^{-1}\) corresponding to \( \nu \text{C–O–C} \).

With regard to the polycomplexes obtained by simple mixing of preformed PVP and PMAA, the FTIR spectra
recorded both before (curve c) and after (curve d) the same thermal treatment show qualitatively similar results to those of the TP complexes. However, it can be observed that in this case, the intensities of the 1750 and 1020 cm\(^{-1}\) peaks are less pronounced with respect to those of the TP complexes, whilst the 1804 cm\(^{-1}\) peak is quite undetectable. This represents a further demonstration that the anhydridization process induced by the thermal treatment is less favoured when the complex formation between PMAA and PVP takes place via simple mixing rather than via TP. A possible explanation could be that by polymerizing MAA onto PVP, most of the neoformed PMAA chains are paired with the PVP chains by hydrogen bonds; therefore, the –COOH groups are arranged in a quite ordered structure that favours them to interact with each other forming the anhydride links. On the contrary, on blending the preformed polymers, the pairing between PMAA and PVP chains is strongly irregular. Therefore, some PMAA and PVP chains remain unpaired and, because of this random structure, the PMAA anhydridization results less pronounced.

4. Conclusions

PVP exerts a template effect on the polymerization of MAA performed in aqueous solution. Considering that weak interactions in the form of hydrogen bonds occur between the two components, it can be supposed that TP proceeds according to a pick-up mechanism. The final reaction product is a PMAA/PVP complex whose properties were studied and compared with those of a similar complex obtained by simple mixing of preformed PVP and PMAA. By subjecting these complexes to a thermal treatment at 200\(^\circ\)C, an inter- and intramolecular anhydridization reaction occurs involving the –COOH groups of PMAA. The results shown by DSC, TGA and FTIR spectroscopy indicate that this reaction is more favoured in the case of the TP complexes than in the SM complexes. Therefore, it can be concluded that using the TP procedure, PMAA/PVP complexes with a more ordered structure can be prepared.

References


Fig. 4. FTIR spectrum of polycomplexes for TP polycomplexes before (a) and after (b) thermal treatment at 200°C for 1 h; for SM polycomplexes before (c) and after (d) treatment at 200°C for 1 h.