European Polymer Journal 59 (2014) 200–207

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Fourier-transform infrared spectroscopic study of a fractional-complexed polymer blend

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ARTICLE INFO

Article history:
Received 10 April 2014
Received in revised form 24 July 2014
Accepted 28 July 2014
Available online 8 August 2014

Keywords:
Miscible blend
Inter-polymer complex
Associative phase separation
Hydrogen bond
FTIR spectroscopy
DFT

ABSTRACT

FTIR spectroscopy and quantum chemical calculations have been used to explore the system of high-molecular mass pair of miscible polymers poly(*N*-methyldodecano-12-lactam) (PMDL) and poly(4-vinylphenol) (PVPh) in tetrahydrofuran (THF) that is known to undergo associative phase separation into a gel-like interpolymer complex and a soluble residual phase (RP). Using quantum chemical calculations, two types of hydrogen bonding interactions involving the C═O group of PMDL and either one or two O—H groups of PVPh were identified in the FTIR spectra of both the complex and RP. Although relatively small differences were found between the FTIR spectra of the complex and RP, detailed analysis of the C═O stretching region revealed that in the complex, the stronger H-bonding interactions of the C═O groups with two O—H groups slightly outnumbered those in RP. In addition, a proof was added to the recent claim that fractionation accompanied the process of H-bond formation and complex precipitation but did not precede it. Finally, it was suggested that change in thermodynamic quality of solvent took place due to the complexation of the two polymers; the complex stability in a polar proton-donating solvent was tested as well.

1. Introduction

One way of developing new materials with optimized properties is to search for such combinations of two polymers that are capable of forming interpolymer complexes [1–3]. Those interpolymer complexes that are formed due to hydrogen bonding are at the extreme of the miscibility scale: the scale starts with completely immiscible blends, which are followed by partially miscible/compatible blends, by miscible blends of various degree of homogeneity, by soluble complex aggregates, and, finally, the scale ends with gel-like interpolymer complexes [4,5], in which the complexation leads to an associative phase separation [6].

Several factors can affect complexation of two miscible polymers in a common solvent: composition, concentration, molecular mass/chain length of polymer components, presence of any steric hindrance, strength of hydrogen-bond interactions. The nature of the solvent must also be taken into account [2,4,7]. In the complexation driven by hydrogen bonding, three types of interaction forces have to be considered: intermolecular H-bonds between the proton-donor and proton-acceptor groups of the two polymers (these favour the complex formation), self-association of the proton-donating polymer due to intramolecular hydrogen bonds (unfavourable to complex formation), and unfavourable interactions between the proton-accepting solvent and proton-donating polymer. A complex can only be formed if the favourable interpolymer interactions prevail [2,4,5,8]. In addition to the hydrogen bonding interactions, the thermodynamic quality of the solvent used may also play a role. Even when the quality of the solvent is good for both constituent

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http://dx.doi.org/10.1016/j.eurpolymj.2014.07.036
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polymers, upon formation of complex the effective solvent quality may change. This could lead to a solvophobic effect [9].

The complexation process is strongly dependent on the molecular mass/chain length of polymer components [1,4,7]. In the studies of systems of two miscible polymers in a common solvent, several authors [4,10,11] found that high-molecular mass (HM) polymers formed a gel-like complex whereas the low-molecular mass (LM) pair formed a soluble blend. In these cases, formation of an interpolymer complex required the chain length exceeding certain critical value. In other cases, the hydrogen bonding interactions between two chosen polymers were optimized when the two polymers had almost the same chain length. When one of the polymers was shorter or longer, it formed self-associates – a process that competed with formation of hydrogen bonds with the second polymer [12].

The gel-like inter-polymer complex is assumed to have a ladder-like structure of co-operative H-bonds, contrary to a loose random H-bond structure of a soluble blend [1,2,4,13]. Such structures can be detected e.g. by the non-radiative energy transfer (NRET) fluorescence spectroscopy [14,15] or dielectric relaxation [16].

Since vibrational frequency of a functional group is sensitive to any involvement of the group in hydrogen bonding interactions, Fourier-Transform Infrared (FTIR) spectroscopy is the technique of choice for the analysis of the interactions between the two chosen polymers [6,8,12,17–21]. However, there are not many publications devoted to direct comparison of FTIR spectra of gel-like complexes and soluble blends. Garay et al. [6] studied blends of poly(*N*-tert-butylacrylamide) (PTBAA) with poly(acrylic acid) (PAA). These polymers formed a soluble blend in ethanol whereas a gel-like complex in 1-propanol. Formation of hydrogen bonds in the PTBAA + PAA complex was indicated in the FTIR spectra by shifts of the amide carbonyl band and of the band of carboxyl acid dimers, while the soluble blend of the same polymers showed no shift of the amide carbonyl band. On the other hand, Liu et al. [10] found no significant difference between the FTIR spectra of the soluble LM blend and the gel-like HM complex in the system poly(*N*-acryoyl-*N*-methylpiperazine + PVPh + ethanol.

PMDL is miscible with PVPh and the blends of the LM pair PMDL + PVPh are soluble in tetrahydrofuran (THF). In our previous study [22], we characterized these blends by differential scanning calorimetry and attenuated-total-reflection FTIR spectroscopy. The miscibility was induced by hydrogen bonds between OH groups of PVPh as a proton donor and CO groups of PMDL as a proton acceptor.

In the first part of our work devoted to complexation in the system PMDL + PVPh + THF [23], we studied the HM pair of these polymers in THF. As the factors influencing miscibility/complexation in the system PMDL + PVPh + THF were the same as in the above mentioned system containing the LM polymer pair (except molecular mass of the polymer components), we expected the process of complexation to be accompanied by fractionation leading to equilibrium between the HM gel-like complex and the LM soluble RP. These two types of associates were characterized by DSC and size exclusion chromatography (SEC). It was found that average molar ratio PMDL:PVPh in the complex was 1:2, which was considered an optimum composition of the inter-polymer complex. The complex showed higher glass-transition temperature T_g and higher thermal stability than RP. Formation of the inter-polymer complex in the studied system and differences in its properties from RP were caused by higher molecular mass/length of associated polymer chains as a result of fractionation during which the high-molecular fractions formed the gel-like inter-polymer complex and the low-molecular fractions formed the soluble RP. We called this process fractional complexation.

Direct comparisons of gel-like complexes and soluble blends are rare and in addition, in such studies the complex and the blend were each prepared under different conditions (solvent, molecular weight). Our system enables such direct comparison since the complex and the blend were both prepared from one solution. In the present study, we carried out ATR FTIR spectroscopy and density functional theory (DFT) calculations to compare the strength and density of hydrogen bonds of the PMDL/PVPh complex with those in RP as well as in the LM polymer pair. The aim of such investigation was to identify the main factors responsible for the differences in behaviour and properties of the LM blend, the HM interpolymer complex and RP as well as to understand better the mechanism of the complex formation. In addition, we explored the stability of the HM complex in the strong H-bond-breaking solvent dimethyl acetamide (DMAA) by means of transmission FTIR spectroscopy in order to corroborate the SEC analysis in the previous study [23].

2. Experimental

2.1. Materials

PMDL was prepared by acid polymerization of *N*-methyldodecano-12-lactam as described elsewhere [24]. PVPh was obtained from Sigma–Aldrich. The molecular mass parameters of both polymers determined by SEC are shown in Table 1 together with T_g values determined by DSC. THF, hexane, and DMAA of p.a. quality were used as purchased. Before any sample preparation, PVPh was dried in a vacuum oven at 140 °C for 24 h. The sample preparation was described in detail in the first part of the study on complexation in the PMDL + PVPh + THF system [23]. Here, we present just a brief excerpt related to the FTIR measurements.

The weight amounts of neat polymers were separately dissolved in THF to 2 wt.% solutions. The solution of PMDL was added drop-wise to the solution of PVPh stirred in a Teflon crucible and the mixture was stirred for 2 h to establish equilibrium. The gel-like complex was

Table 1
Characteristics of polymers used.

	M_n (Da)	M_w (Da)	M_w/M_n	T_g (°C)
PMDL	41,450	68,150	1.64	−26.7
PVPh	19,700	40,900	2.08	179.6