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Synthesis of hydrogenated functional polynorbornene (HFPNB) and rheology of HFPNB-based miscible blends with hydrogen bonding

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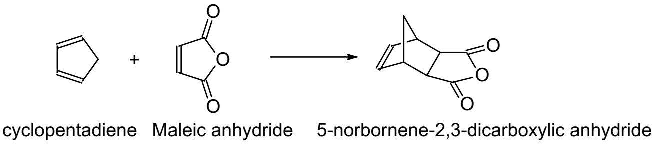
ABSTRACT

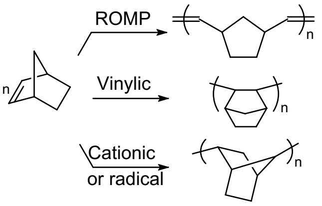
Hydrogenated functional polynorbornene (HFPNB) was first synthesized and then it was used to investigate the rheology of HFPNB-based miscible blends with hydrogen bonding. For the investigation, functional norbornene with carboxylic (–COOH) group was first synthesized and then it was polymerized, via ring-opening metathesis polymerization followed by hydrogenation, to obtain hydrogenated functional polynorbornene (HFPNB), HPNBCOOH. Subsequently, the miscibility of binary blends consisting of (1) HPNBCOOH and polycarbonate (PC) and (2) HPNBCOOH and poly(2-vinylpyridine) (P2VP) was investigated using differential scanning calorimetry (DSC). It has been found that both PC/HPNBCOOH and P2VP/HPNBCOOH blend systems exhibit a broad, single glass transition over the entire range of blend compositions as determined by DSC, indicating that the respective blend systems are miscible, and they were found to form hydrogen bonds as determined by Fourier transform infrared (FTIR) spectroscopy. The dynamic oscillatory shear rheometry has shown that reduced $\log G'$ versus $\log a_T\omega$ and $\log G''$ versus $\log a_T\omega$ plots with a_T being a temperature-dependent shift factor of PC/HPNBCOOH and P2VP/HPNBCOOH blend systems, respectively, are independent of temperature. Further, $\log G'$ versus $\log G''$ plots for both blend systems were also found to be independent of temperature. These observations indicate that an application of time–temperature superposition to the PC/HPNBCOOH and P2VP/HPNBCOOH miscible blend systems with hydrogen bonding is warranted although the difference in component glass transition temperature is as large as 91 °C for PC/HPNBCOOH blends, leading us to conclude that concentration fluctuations and dynamic heterogeneity in the HPBNCOOH-based miscible blend systems might be insignificant.

1. Introduction

Norbornene has received much attention since it can easily be functionalized. Functionalized norbornenes are prepared by Diels–Alder reactions. For example, 5-norbornene-2,3-dicarboxylic anhydride can be prepared via the Diels–Alder reaction between cyclopentadiene and maleic anhydride, as shown below [1].



Norbornene and its derivatives have been polymerized in three different ways: (1) ring-opening metathesis polymerization (ROMP), (2) vinylic polymerization, and (3) radical or cationic polymerization, as schematically shown below.



The structure and properties of the polynorbornene (PNB) are dependent upon the type of catalyst used. By free-radical or cationic polymerization, 2,7-connected PNB is obtained [2–4]. The initiators commonly used for the free-radical polymerization are azoisobutyronitrile (AIBN), *tert*-butyl peracetate, or *tert*-butyl perpivalate. The cationic polymerization of norbornene can be conducted using $EtAlCl_2$ as initiator. The polymers synthesized by cationic polymerization yield low molecular weights. In 1967 the vinylic polymerization of norbornene with palladium(II) catalysts was patented [5]. The vinylic polymerization is conducted by

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opening only the double bond of the π-component and leaving the bicyclic structural unit intact. The PNBs synthesized by vinylic polymerization are saturated 2,3-inserted rotationally constrained polymers, exhibiting a high density, high chemical resistance, high refractive index, low birefringence, etc.[6–8].

In the past, numerous research groups investigated the ROMP of norbornene and the efforts are summarized in a monograph [9]. ROMP is an efficient method for synthesizing polymers with a rather narrow molecular weight distribution owing to its living nature. PNB synthesized via ROMP was first developed by CdF Chemie/Nippon Zeon in the late 1970s using a tungsten–carbene complex as catalyst. This polymer has been commercialized with the trade name Norsorex™. Being a linear amorphous polymer, Norsorex™ has been used as an elastomer [10,11], which contains 70–80 mol% *trans*-linked norbornene units, has a molecular weight of about 3×10^6 and a glass transition temperature between 35 and 45 °C [12–14].

PNBs with functional groups usually are obtained via ROMP of the corresponding norbornene derivatives [15–21]. However, it has been reported that some functional groups such as hydroxyl and carboxylic groups would decrease the reactivity of the catalysts used for ROMP [22]. As a result, PNBs with those functional groups should be obtained via alternative methods. Therefore, appropriate methods must be taken to protect such functional groups before polymerization.

Depending on the type of substituent group(s) in norbornene, the properties of the resultant PNBs vary over a wide range, say from rubberlike to highly rigid materials. In this regard, PNB can be regarded as an intermediate between elastomers and thermoplastics [23]. Schrock and coworkers [24–28] synthesized, via ROMP of norbornene derivatives, norbornene-containing side-chain liquid-crystalline polymers (SCLCP). They investigated the effects of molecular weight, polydispersity, and the number of methylene flexible spacers ($n = 2$–12) on the thermotropic behavior of SCLCPs.

To date, only a few research groups have reported on PNB-based thermoplastic blends. Kokuryo [29] reported on blends of PNB with poly(vinyl chloride) (PVC), polystyrene (PS), poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS), and polycarbonate (PC). It is very doubtful that PNB/PVC, PNB/PS, PNB/ABS, and PNB/PC pairs can form miscible blends because PNB does not have any functional group that may have attractive interactions with PVC, PS, ABS, or PC.

The present study was motivated by the following considerations. Norbornene is one of the few monomers that can easily be functionalized with a variety of functional groups. With this understanding, we synthesized functionalized PNBs by first functionalizing norbornene with carboxylic groups and then followed by hydrogenation to obtain hydrogenated PNB with carboxylic groups (HPNBCOOH). Hydrogenation was necessary because, without hydrogenation, PNBCOOH is thermally very unstable. We then mixed HPNBCOOH with polycarbonate (PC) or poly(2-vinylpyridine) (P2VP) to prepare PC/HPNBCOOH and P2VP/HPNBCOOH blends, each being expected to form hydrogen bonds. The purpose of the preparation of those polymer blends was to investigate the rheological behavior of miscible polymer blends with hydrogen bonding. Indeed we confirmed, via Fourier transform infrared (FTIR) spectroscopy, the formation of hydrogen bonds in each of the two blend systems prepared. Subsequently, we investigated the linear dynamic viscoelasticity of the miscible polymer blends with hydrogen bonding. In this paper we will report the highlights of our findings from the study.

2. Experimental

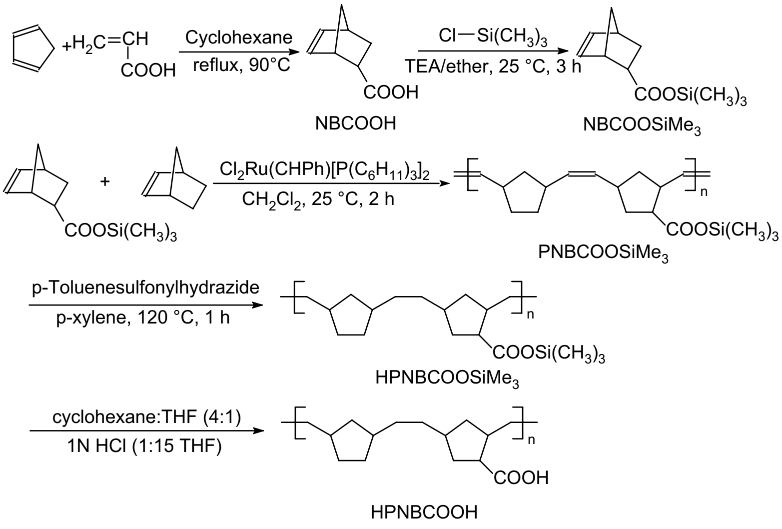
2.1. Materials

All chemicals were used as received without purification unless otherwise mentioned. Bis(tricyclohexyl phosphine)-benzylidene-ruthenium dichloride (Grubbs catalyst I) was purchased from Strem. Dicyclopentadiene, acrylic acid, trimethylchlorosilane, triethylamine (TEA), norbornene (NB), *p*-toluenesulfonylhydrazide (TSH), and lithium aluminum hydride ($LiAlH_4$) were purchased from Aldrich. Solvents such as *p*-xylene and tetrahydrofuran (THF) were purified by usual procedures and handled under a moisture-free atmosphere. Methylene chloride, used as a solvent for polymerization, was dried over calcium hydride and distilled before use. Polycarbonate (PC) (22MFR), used for preparing blends with HPNBCOOH, was supplied by Dow Chemical Company.

2.2. Synthesis of polymers

2.2.1. Synthesis of hydrogenated polynorbornene with carboxylic acid group (HPNBCOOH)

The reaction scheme for the synthesis of HPNBCOOH is shown in Scheme 1. First, 5-norbornene-2-carboxylic acid was prepared by the Diels–Alder reaction of acrylic acid and cyclopentadiene (CPD) in cyclohexane as follows. First, cyclopentadiene was prepared via the fractional distillation of dicyclopentadiene. Heat was applied



Scheme 1. Synthesis route for HPNBCOOH.

continuously to promote rapid distillation without exceeding the boiling point of 42 °C. Freshly cracked cyclopentadiene in an ice-cooled receiver was obtained. The reaction mixture of cyclopentadiene and acrylic acid in cyclohexane was stirred at 90 °C for 12 h. The acids produced were separated from cyclohexane (and the slight excess of cyclopentadiene) by extraction with aqueous sodium hydroxide (10% NaOH), followed by acidification (20% hydrochloric acid, HCl), extraction with chloroform, drying with magnesium sulfate, and distillation under vacuum (b.p. 134 °C/16 mm Hg). The product was crystallized in the receiver as colorless needles.

It is reported that carboxylic acid group in norbornene will reduce the reactivity of ROMP catalyst [22]. As a result, PNB with carboxylic acid groups could not be obtained directly from ROMP of 5-norbornene-2-carboxylic acid. A suitable protection group was needed to protect the carboxylic acid group. In this study we used trimethylsiloxy as a protection group [30]. 5-Norbornene-2-trimethylsiloxy ester ($NBCOOSiMe_3$) was synthesized as follows.

5-Norbornene-2-carboxylic acid was reacted with trimethylchlorosilane and triethylamine in diethyl ether at room temperature. The reaction product was distilled under vacuum (44–46 °C/2 mm Hg) to obtain a colorless oil.

To control the content of carboxylic acid, a copolymer of norbornene and 5-norbornene-2-trimethylsiloxy ester was synthesized. ROMP was carried out using the Grubbs metathesis catalyst $\{Cl_2Ru(CHPh)[P(C_6H_{11})_3]_2\}$ under oxygen-free conditions in anhydrous methylene chloride. The reaction was carried out at 25 °C for 2 h and was terminated by the addition of a small amount of ethyl vinyl ether. The copolymer was then precipitated in excess methanol. The copolymer was further purified by dissolving it in THF and re-precipitating it with methanol, and then dried overnight in a vacuum oven at room temperature.

To improve the thermal stability and anti-ozone ability of functionalized polynorbornenes, the C=C double bonds in PNBs were hydrogenated using the following procedures. Poly(5-norbornene-2-trimethylsiloxy methylene) and *p*-toluenesulfonylhydrazide (TSH) were mixed in anhydrous *p*-xylene and heated for 1 h at 120 °C under a nitrogen atmosphere. Complete solubilization of the mixture was achieved by the time when the temperature reached 100 °C. The onset of the reaction was marked by the vigorous evolution of gas. After the reaction was completed, hydrochloric acid was added to remove the protection groups. The mixture was then allowed to cool and poured into methanol. The hydrogenated polymer was collected on a Teflon filter, washed with methanol several times, and then dried under vacuum. A copolymer was hydrolyzed by adding THF and 1 N HCl and allowing the mixture to stand at room temperature for 3 h. The copolymer was then precipitated in excess methanol and dried overnight in a vacuum oven at room temperature.

2.2.2. *Synthesis of poly(2-vinyl pyridine) (P2VP)*

2-Vinylpyridine (2-VP) dried with potassium hydroxide and distilled in vacuum was sealed in ampoules with calcium hydride. Before polymerization it was vacuum-distilled. Radical polymerization of 2-VP was carried out with AIBN as an initiator in toluene at 65 °C for 24 h. The polymerization was stopped by pouring the solution into ether. The crude polymer was then dissolved in methanol and precipitated into ether. The polymer thus obtained was dried in a vacuum oven at 50 °C. The chemical structure of P2VP was confirmed using FTIR spectroscopy.

2.3. *Preparation of miscible polymer blends*

Samples for differential scanning calorimetry (DSC), FTIR, and rheological experiments were prepared by solvent casting. Blends of different compositions were prepared by dissolving a predetermined amount of the constituent components in THF (5% solids in solution) in the presence of 0.1 wt% antioxidant (Irganox 1010, Ciba-Geigy Group). The solution was kept at room temperature for 24 h in a fume hood to allow for evaporation of most of the solvent. Following this, they were freeze-dried at room temperature for 3 days under vacuum and dried further at a temperature near T_g for 2 days under vacuum. The dried sample was compression molded and annealed at $T_g + 20$ °C in a vacuum oven.

2.4. *Thermal analysis and structural characterization of the polymers synthesized*

The glass transition temperature (T_g) was determined by DSC (TA instrument or Perkin–Elmer DSC-7) at a heating rate of 20 °C/min. DSC thermograms were recorded and T_g is taken as the midpoint of the transition in the second scan. The thermal decomposition temperature was determined by thermo gravimetric analysis (TGA) (TA instrument) to ensure that materials would not degrade over the range of temperatures employed for rheological measurements.

Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (200 MHz Varian Gemini-200 spectrometer) was used to determine the chemical structures of the polymers synthesized. A Fourier transform infrared spectrometer (Perkin–Elmer 16PC) was used to record infrared (IR) spectra of the polymers synthesized and 16 scans were collected with a spectral resolution of 4 cm^{-1}. The solution (2% w/v) containing the blend was cast onto a potassium bromide (KBr) disk. Film thickness was adjusted, such that the maximum absorbance of any band was less than 1.0 at which the Beer–Lambert law is valid. It was slowly dried for 24 h in a fume hood until most of the solvent evaporated and then dried at 50 °C for a few days in a vacuum oven. Samples were then stored in a desiccator until use.

Gel permeation chromatography (GPC) measurements were performed on a Waters GPC equipped with Ultrastyragel columns using THF as an elution solvent at a rate of 1 mL/min. Monodisperse polystyrenes were used as calibration standards.

2.5. *Oscillatory shear rheometry*

Rheological experiments were conducted using an Advanced Rheometrics Expanded System (ARES, TA Instruments) in the oscillatory mode with the parallel-plate fixture (8 mm diameter). For the experiments, the dynamic storage and loss moduli (G' and G'') were measured as functions of angular frequency (ω) ranging from 0.04 to 100 rad/s at various temperatures during heating. The measurement temperature was varied depending on the T_g of the specimen (from T_g +30 °C to +80 °C). All the measurements were conducted under a nitrogen atmosphere in order to avoid oxidative degradation of the samples.

3. Results and discussion

3.1. *Structural characterization*

3.1.1. *HPNBCOOH*

Fig. 1 gives the FTIR spectra of (a) 5-norbornene-2-carboxylic acid (NBCOOH) and (b) 5-norbornene-2-trimethylsiloxy ester ($NBCOOSiMe_3$). In Fig. 1a the absorption peak at 1700 cm^{-1} corresponds to the vibration of carbonyl group (C=O), and a broad band between 2500 and 3500 cm^{-1} represents the carboxylic acid group. In Fig. 1b we observe that the carboxylic peak at 1700 cm^{-1} and a very broad peak centered at 3000 cm^{-1} disappear, and the ester peak at 1740 cm^{-1} appears. Also, in Fig. 1b the absorptions of CH_3 symmetric bending of Si–CH_3 at 1254 cm^{-1}, CH_3 asymmetric

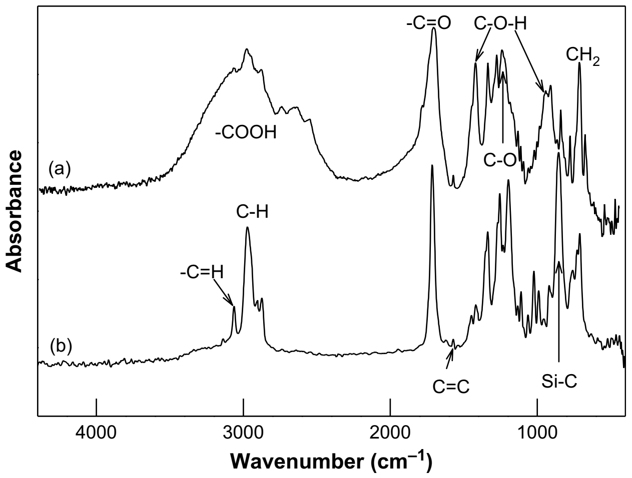


Fig. 1. FTIR spectra of (a) NBCOOH and (b) NBCOOSiMe$_3$.

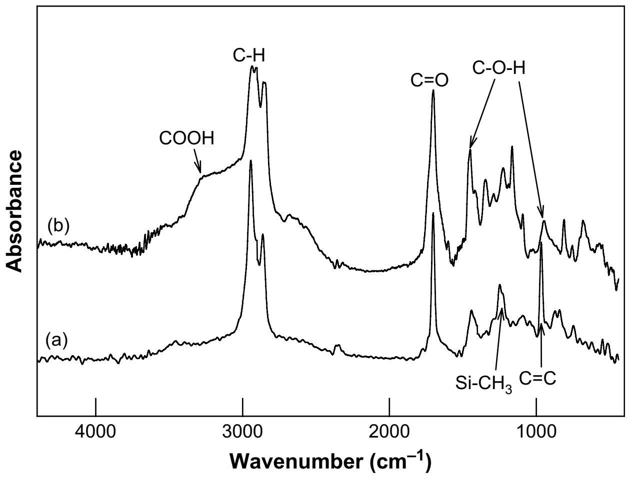


Fig. 3. FTIR spectra of (a) PNBCOOSiMe$_3$ and (b) HPNBCOOH.

bending of Si–CH$_3$ at 1418 cm^{-1}, and Si–C stretching at 854 cm^{-1} appear [31,32]. These observations indicate that the carboxylic acid group was protected in NBCOOSiMe$_3$.

Fig. 2 gives the ^{1}H NMR spectra of (a) NBCOOH and (b) NBCOOSiMe$_3$. In Fig. 2a we observe that the strong absorption peak at $\delta = 5.7$–6.0 ppm represents C=C double bonds, and a weak absorption peak at $\delta = 11.8$ ppm represents the carboxylic acid group (–COOH). The ^{1}H NMR spectra in Fig. 2b show an absorption peak at $\delta = 0.08$ ppm for Si–CH$_3$ vibration, indicating the formation of NBCOOSiMe$_3$. Thus, combining the FTIR and ^{1}H NMR spectra we confirm that 5-norbornene-2-carboxylic acid has the right chemical structure as we expected.

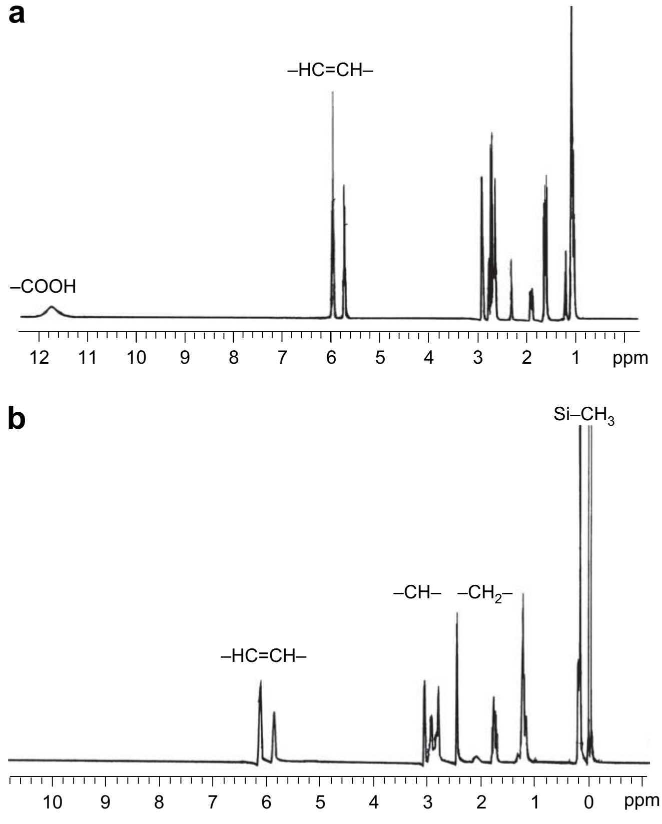


Fig. 2. ^{1}H NMR spectra of (a) NBCOOH and (b) NBCOOSiMe$_3$ in DMSO.

After polymerization, the functionalized polynorbornene PNBCOOSiMe$_3$ was hydrogenated yielding HPNBCOOSiMe$_3$ and then –COOSiMe$_3$ group in HNBCOOSiMe$_3$ was unprotected yielding HPNBCOOH. Fig. 3 gives the FTIR spectra of PNB (a) before hydrogenation and (b) after hydrogenation followed by removal of trimethylsiloxy protection group. It can be seen from Fig. 3b that a broad band corresponding to carboxylic acid group at 2500–3500 cm^{-1} appears again (compare with Fig. 3a) and the absorption band assigned to Si–CH$_3$ at 1254 cm^{-1} disappears, indicating that the trimethylsiloxy protection group was removed. Also, the absorption band at 968 cm^{-1} assigned to the C–H bonds adjacent to *trans* double bonds is totally absent from the spectrum, indicating that the PNBCOOH was totally hydrogenated yielding hydrogenated HPNBCOOH. Fig. 4 gives the ^{1}H NMR spectra of HPNBCOOH, in which we observe no olefinic resonance visible after hydrogenation. That is, after hydrogenation no absorption peak appears in Fig. 4 at $\delta = 5.6$–6.0 ppm, which appeared before hydrogenation as shown in Fig. 2a. Thus, we have confirmed, via FTIR and ^{1}H NMR spectroscopies, the chemical structure of the hydrogenated polynorbornene with carboxylic acid groups, HPNBCOOH.

3.1.2. Molecular characteristics of PNB

The effects of the amount of catalyst used and the duration of reaction on molecular weight was investigated and the results are summarized in Table 1. It can be seen in Table 1 that for a longer period (60 min) of reaction, a high-molecular-weight ($M_w = 2 \times 10^5$) PNB with a relatively narrow polydispersity (1.22) was obtained when 0.1 wt% of catalyst was employed. However, when the duration of reaction was shortened to 20 min with the same amount of catalyst (0.1 wt%), a low-molecular-weight

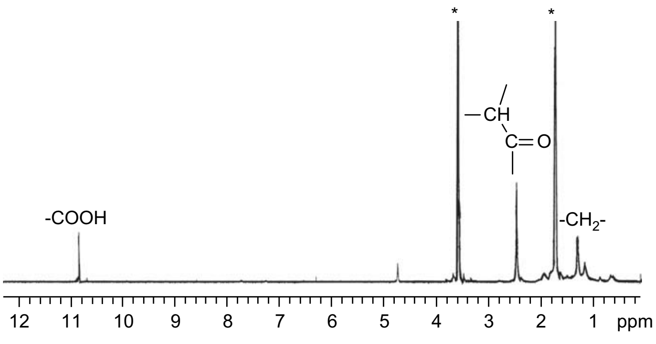


Fig. 4. ^{1}H NMR spectrum of HPNBCOOH in deuterated THF.

Table 1
Molecular characterization of the PNBs synthesized in this study

Reaction period (min)	Catalyst added (wt%)	Measured M_w	Calculated M_w	M_w/M_n
20	0.1	2.3×10^4	1.8×10^5	1.51
60	0.1	2.0×10^5	1.8×10^5	1.22
60	1.0	2.3×10^4	1.5×10^4	1.19
60	0.5	4.6×10^4	3.0×10^4	1.07

($M_w = 2.3 \times 10^4$) PBN was obtained and the yield was only 10% and the polydispersity became broader (1.51). On the other hand, when the amount of catalyst was increased to 1 wt% with the duration of reaction for 60 min, the molecular weight was decreased. For example, when 1 wt% of catalyst was used, the molecular weight was 2.3×10^4. All these features are consistent with the living nature of ROMP.

The thermal stability of the polymers synthesized was found to be relatively poor. The thermal degradation temperature of HPNBCOOH was found to be only 140 °C, which is the onset point of anhydride formation for carboxylic acid group. As a result, later we could not run rheological measurements at temperatures higher than 140 °C for HPNBCOOH.

3.2. Miscibility of functionalized polynorbornene-based blend

3.2.1. Miscibility of PC/HPNBCOOH blends

Blends of HPNBCOOH and PC were prepared by dissolving both components in THF. Fig. 5a gives DSC thermograms at a heating rate of 20 °C/min of PC/HPNBCOOH blend system, showing a broad, single glass transition for each blend composition, in which the upward arrow denotes the onset point (T_{gi}), the symbol + denotes the midpoint (T_{gm}), and the downward arrow denotes the end point (T_{ge}) of the glass transition. A single, though broad, glass transition indicates that the blends are miscible over the entire blend composition. Table 2 gives a summary of the values of T_{gi}, T_{gm}, and T_{ge}. Also given in Table 2 is the width of glass transition, $\Delta w_{T_g} = T_{ge} - T_{gi}$, for each blend composition. Note that in Table 2 the difference in component glass transition temperature, ΔT_g, is 91 °C and Δw_{T_g} is about 20 °C, which is larger than that (~10 °C) of the constituent components. Fig. 5b gives composition dependence of T_{gm} for PC/HPNBCOOH blends, showing negative deviation from linearity. Earlier, negative deviation from linearity in the plots of T_g versus blend composition was also observed for miscible blends of poly(*N*-vinylpyrrolidone) and poly[ethylene-*co*-(acrylic acid)] forming hydrogen bonds [33] and for miscible blends of poly(vinylphenol) and poly(L-lactide) forming hydrogen bonds [34]. It was suggested [35,36] that negative deviation from linearity in the plot of T_g versus blend composition indicates that the strength of attractive interactions between the constituent components of miscible polymer blends is not strong.

Fig. 6 gives the FTIR spectra of the carbonyl stretching (1650–1750 cm^{-1}) vibration region for PC/HPNBCOOH blends. It can be seen that there are two carbonyl bands: one assigned to the hydrogen-bonded carboxylic acid dimers at 1700 cm^{-1} and another assigned to the hydrogen bonds formed between the –COOH groups in HPNBCOOH and the carbonyl groups in PC at 1730 cm^{-1}. The absorption band at 1730 cm^{-1} is not very obvious, indicating that the specific interaction between PC and HPNBCOOH is not strong.

3.2.2. Miscibility of P2VP/HPNBCOOH blends

Blends of HPNBCOOH with P2VP were prepared by dissolving both components in pyridine. Fig. 7a gives DSC thermograms at a heating rate of 20 °C/min of the P2VP/HPNBCOOH blend system, showing a broad, single glass transition for each blend composition.

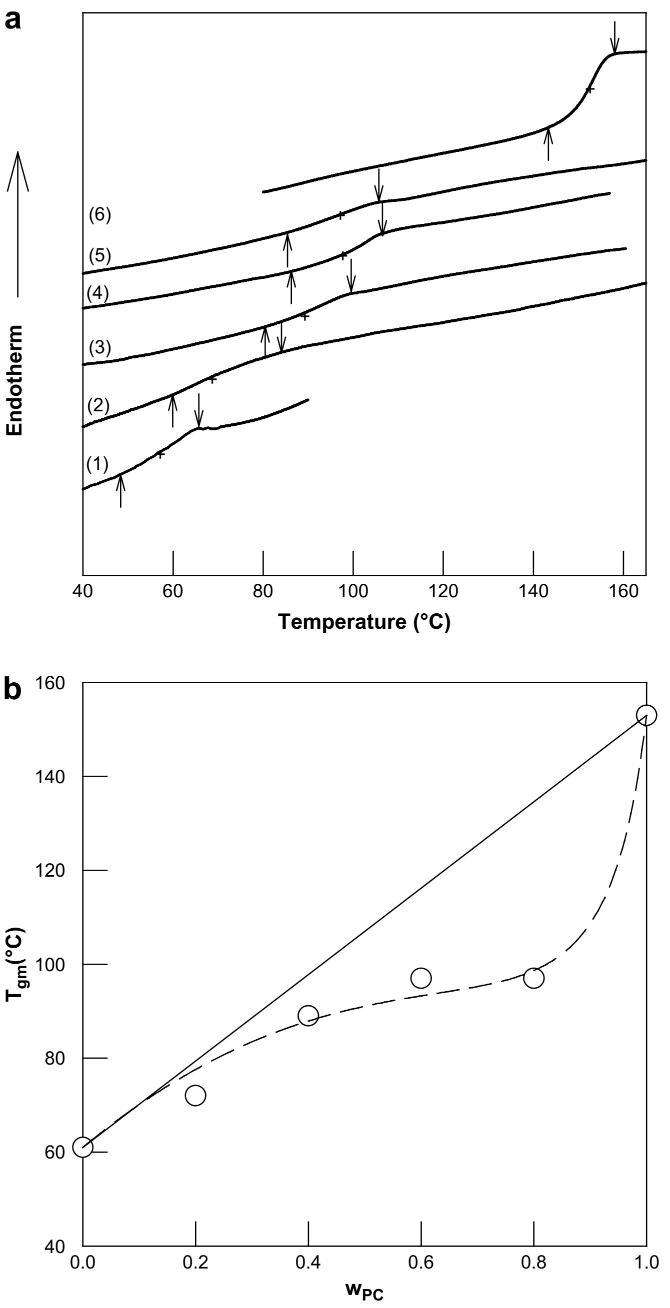


Fig. 5. (a) DSC thermograms of PC/HPNBCOOH blends during heating at a rate of 20 °C/min: (1) HPNBCOOH, (2) 20/80 PC/HPNBCOOH blend, (3) 40/60 PC/HPNBCOOH blend, (4) 60/40 PC/HPNBCOOH blend, (5) 80/20 PC/HPNBCOOH blend, and (6) PC; (b) composition-dependent glass transition temperature T_{gm} for PC/HPNBCOOH blends.

The DSC thermograms indicate that the blends are miscible over the entire blend composition. Table 3 gives a summary of the values of T_{gi}, T_{gm}, T_{ge}, and Δw_{T_g} of the P2VP/HPNBCOOH blend system, showing that ΔT_g is 36 °C and Δw_{T_g} is about 20 °C. Fig. 7b gives composition dependence of T_{gm} for P2VP/HPNBCOOH blends, showing small negative deviation from linearity. This observation indicates that the strength of attractive interactions between P2VP and HPNBCOOH is stronger than that between PC and HPNBCOOH (compare Fig. 7b with Fig. 5b).

Fig. 8 gives FTIR spectra in the 1500–1800 cm^{-1} range of P2VP/HPNBCOOH blends with various compositions. The absorption band at 1700 cm^{-1} is assigned to the hydrogen-bonded carboxylic acid dimers. As the concentration of HPNBCOOH is increased in

Table 2
Summary of the glass transition temperature of PC/HPNBCOOH blends

Sample code	T_{go} (°C)	T_{gm} (°C)	T_{ge} (°C)	Δw_{T_g} (°C)
HPNBCOOH	56	61	66	10
20/80	61	72	84	23
40/60	79	92	100	21
60/40	85	97	106	21
80/20	84	97	104	20
PC	147	153	156	9

the blend, the absorption bands of pyridine groups in P2VP shift from 1590 to 1600 cm^{-1}, which is attributed to the attractive interactions between the pyridine group in P2VP and the –COOH group in HPNBCOOH [37,38]. Also, the absorption band at 1725 cm^{-1} is assigned to the "free" carbonyl group liberated when the hydrogen bonding between the hydroxyl group and the pyridine group is formed. On the basis of the above observation we conclude that the intermolecular hydrogen bonds were formed between the –COOH groups in HPNBCOOH and the pyridine groups in P2VP.

3.3. *Rheology of HPNBCOOH-based blends*

Since the onset of anhydride formation for carboxylic acid group is about 140 °C, the range of temperatures for rheological measurements taken was limited to a relatively narrow range.

3.3.1. *Rheology of PC/HPNBCOOH blends*

Fig. 9 gives log G' versus log $a_T\omega$ and log G'' versus log $a_T\omega$ plots for 20/80 and 40/60 PC/HPNBCOOH blends at various temperatures, in which values of temperature-dependent shift factor a_T were obtained by shifting log G'' versus log ω plots along the ω axis using $T_r = T_{gm} + 50$ °C as a reference temperature. For the reasons that PC/HPNBCOOH blends undergo thermal degradation at 140 °C and the PC/HPNBCOOH blends having more than 40 wt% PC has a glass transition temperature (T_{ge}) of about 100 °C (see Table 2), we could not carry out rheological measurements for 60/40 and 80/20 PC/HPNBCOOH blends. It can be seen in Fig. 9 that the reduced plots are virtually independent of temperature over the entire range of temperatures tested. Notice, however in Fig. 9 that the slope of

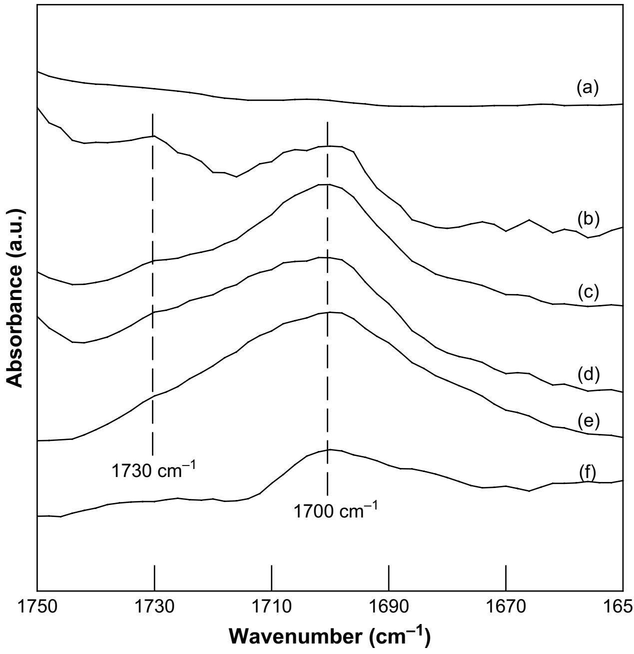


Fig. 6. FTIR spectra of PC/HPNBCOOH blends in the carbonyl stretching region at room temperature: (a) PC, (b) 80/20 PC/HPNBCOOH blend, (c) 60/40 PC/HPNBCOOH blend, (d) 40/60 PC/HPNBCOOH blend, (e) 20/80 PC/HPNBCOOH blend, and (f) HPNBCOOH.

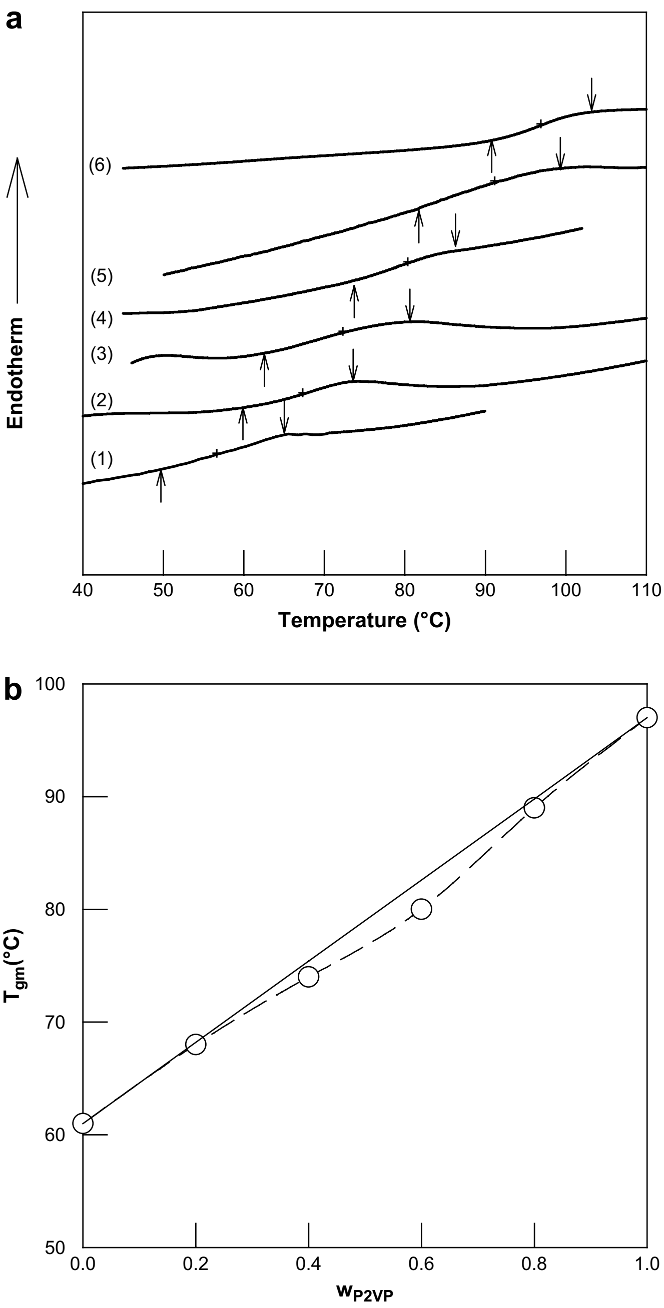


Fig. 7. (a) DSC Thermograms of P2VP/HPNBCOOH blends during heating at a rate of 20 °C/min: (1) HPNBCOOH, (2) 20/80 P2VP/HPNBCOOH blend, (3) 40/60 P2VP/HPNBCOOH blend, (4) 60/40 P2VP/HPNBCOOH blend, (5) 80/20 P2VP/HPNBCOOH blend, and (6) P2VP; (b) composition dependence of T_{gm} for P2VP/HPNBCOOH blends.

Table 3
Summary of the glass transition temperature of P2VP/HPNBCOOH blends

Sample code	T_{go}	T_{gm}	T_{ge}	Δw_{T_g}
HPNBCOOH	56	61	66	10
20/80	59	68	76	17
40/60	62	74	83	21
60/40	72	80	88	16
80/20	81	89	100	19
P2VP	90	97	101	11

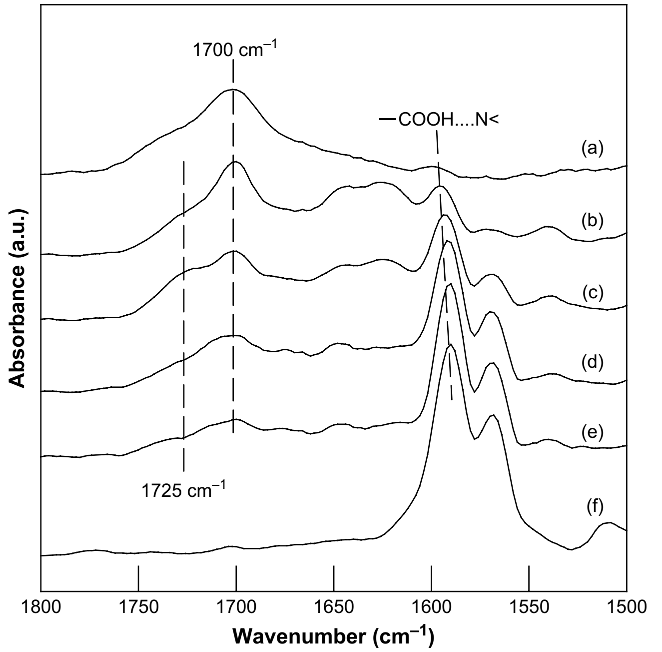


Fig. 8. FTIR spectra in the range of 1500–1800 cm^{-1} for P2VP/HPNBCOOH blends at room temperature: (a) HPNBCOOH, (b) 20/80 P2VP/HPNBCOOH blend, (c) 40/60 P2VP/HPNBCOOH blend, (d) 60/40 P2VP/HPNBCOOH blend, (e) 80/20 P2VP/HPNBCOOH blend, and (f) P2VP.

log G' versus log $a_T\omega$ plots in the terminal region is much smaller than 2, and the slope of log G'' versus log $a_T\omega$ plots in the terminal region is much smaller than 1. We attribute this observation to the presence of hydrogen bonding between the –COOH groups in HPNBCOOH and the carbonyl groups in PC. Miscible polymer blends without hydrogen bonding are expected to exhibit a slope very close to 2 in log G' versus log $a_T\omega$ plots in the terminal region, and the slope of log G'' versus log $a_T\omega$ plots in the terminal region would be very close to 1.

Fig. 10 gives log G' versus log G'' plots for 20/80 and 40/60 PC/HPNBCOOH blends at various temperatures. The following observations are worth noting in Fig. 10. The log G' versus log G'' plots for both blends are virtually independent of temperature over the entire range of temperatures tested, but the slope of the plots for the 40/60 PC/HPNBCOOH blend is less than that for the 20/80 PC/HPNBCOOH blend. This is attributed to the fact that as the amount of PC in the blend is increased from 20 to 40 wt%, the extent of intermolecular attractive interactions between the –COOH groups in HPNBCOOH and the carbonyl groups in PC becomes stronger. On the basis of Figs. 9 and 10 we can conclude that time–temperature superposition (TTS) is applicable to PC/HPNBCOOH blends with hydrogen bonding. It is worth noting that in Fig. 10 the slope of log G' versus log G'' plots in the terminal region is much less than 2, which is attributed to the presence of hydrogen bonds between the –COOH groups in HPNBCOOH and the carbonyl groups in PC. It has been observed that the slope of log G' versus log G'' plots in the terminal region is 2 (or very close to 2) for monodisperse homopolymers [39–41], block copolymers in the disordered state [42–44], liquid-crystalline polymers in the isotropic state [45–47], and miscible polymer blends without specific interactions [48].

3.3.2. Rheology of P2VP/HPNBCOOH blends

Fig. 11 gives log G' versus log $a_T\omega$ and log G'' versus log $a_T\omega$ plots for 20/80, 40/60, 60/40, and 80/20 P2VP/HPNBCOOH blends at various temperatures, in which $T_r = T_{gm} + 50$ °C was used as a reference temperature. The following observations are worth noting in Fig. 11. In all four compositions of P2VP/HPNBCOOH blends both log G' versus log $a_T\omega$ and log G'' versus log $a_T\omega$ plots are independent of temperature, very similar to the observations made for PC/HPNBCOOH blends (see Fig. 9).

While the slope of log G' versus log $a_T\omega$ plots in the terminal region is much less than 2, the degree of the deviation from 2 in the slope of log G' versus log $a_T\omega$ plots in the terminal region varies with blend composition. Specifically, the slope of log G' versus log $a_T\omega$ plots in the terminal region for the 60/40 P2VP/HPNBCOOH blend is less than that for the 40/60 P2VP/HPNBCOOH blend. This observation is attributable to the stronger intermolecular interactions between the pyridine group of P2VP and the –COOH groups in HPNBCOOH in the 60/40 P2VP/HPNBCOOH blend than in the 40/60 P2VP/HPNBCOOH blend. Interestingly, Fig. 11 shows that the slope of log G' versus log $a_T\omega$ plots in the terminal region for the 80/20 P2VP/HPNBCOOH blend is larger than that for the 60/40 P2VP/HPNBCOOH blend. Again, this observation is attributable to the weaker intermolecular interactions between the pyridine group of P2VP and the –COOH groups in HPNBCOOH in the 80/20 P2VP/HPNBCOOH blend than in the 60/40 P2VP/HPNBCOOH blend. This

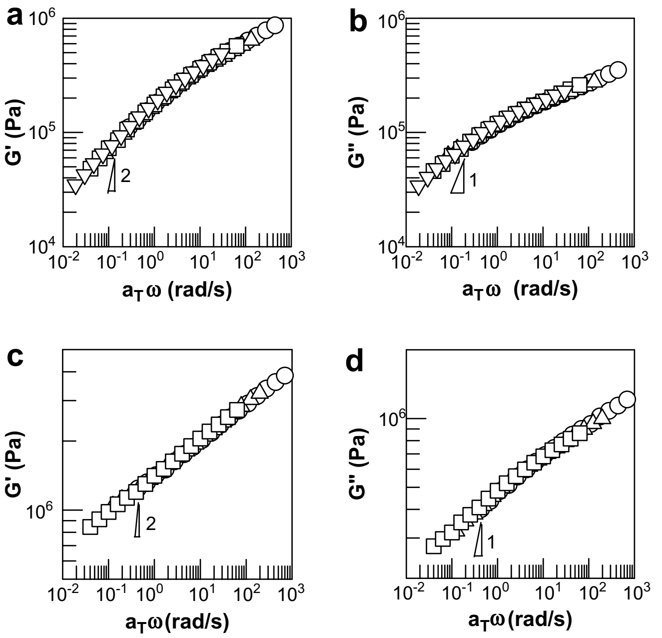


Fig. 9. Plots of log G' versus log $a_T\omega$ and log G'' versus log $a_T\omega$ for PC/HPNBCOOH blends at various temperatures with $T_r = T_{gm} + 50$ °C as the reference temperature: (a) and (b) 20/80 PC/HPNBCOOH blend: (○) 102 °C, (△) 112 °C, (□) 122 °C, and (▽) 132 °C; (c) and (d) 40/60 PC/HPNBCOOH blend: (○) 122 °C, (△) 132 °C, and (□) 142 °C.

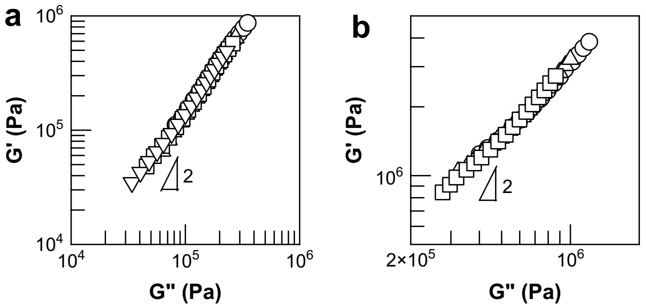


Fig. 10. Plots of log G' versus log G'' for PC/HPNBCOOH blends at various temperatures: (a) 20/80 PC/HPNBCOOH blend: (○) 102 °C, (△) 112 °C, (□) 122 °C, and (▽) 132 °C; (b) 40/60 PC/HPNBCOOH blend: (○) 122 °C, (△) 132 °C, and (□) 142 °C.

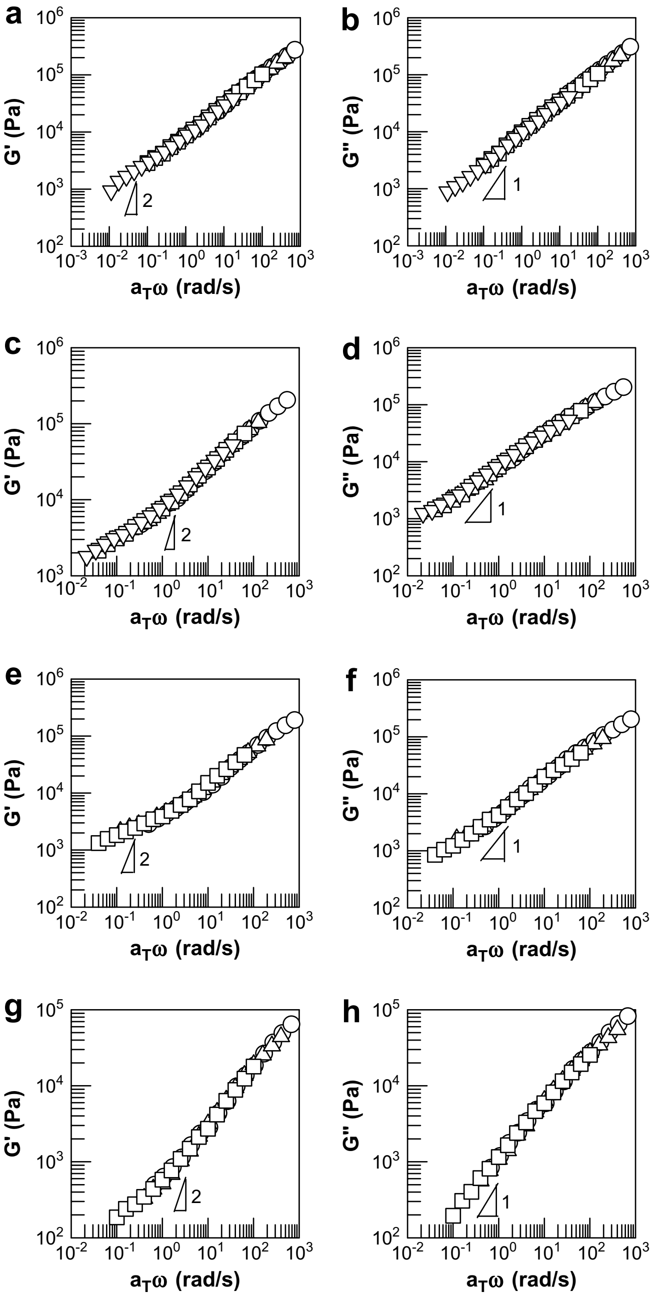


Fig. 11. Plots of log G' versus log $a_T\omega$ and log G'' versus log $a_T\omega$ for P2VP/HPNBCOOH blends at various temperatures with $T_r = T_{gm} + 50$ °C as the reference temperature: (a) and (b) 20/80 P2VP/HPNBCOOH blend: (○) 98 °C, (△) 108 °C, (□) 118 °C, and (▽) 128 °C; (c) and (d) 40/60 P2VP/HPNBCOOH blend: (○) 104 °C, (△) 114 °C, (□) 124 °C, and (▽) 134 °C; (e) and (f) 60/40 P2VP/HPNBCOOH blend: (○) 110 °C, (△) 120 °C, and (□) 130 °C; (g) and (h) 80/20 P2VP/HPNBCOOH blend: (○) 119 °C, (△) 129 °C, and (□) 139 °C.

is because a smaller amount of HPBNCOOH is surrounded by a larger amount of strongly polar P2VP in the 80/20 P2VP/HPNBCOOH blend and thus a lower degree of hydrogen bonding occurred in the blend. It is interesting to observe that the slope of log G' versus log $a_T\omega$ plots in the terminal region for the 20/80 P2VP/HPNBCOOH blend (see Fig. 11a) is less than that for the 80/20 P2VP/HPNBCOOH blend (see Fig. 11g). This is attributable to the presence of hydrogen-bonded carboxylic acid dimers (see Fig. 6) when a larger amount (80 wt%) of HPNBCOOH is surrounded by a smaller amount (20 wt%) of P2VP in the 20/80 P2VP/HPNBCOOH blend.

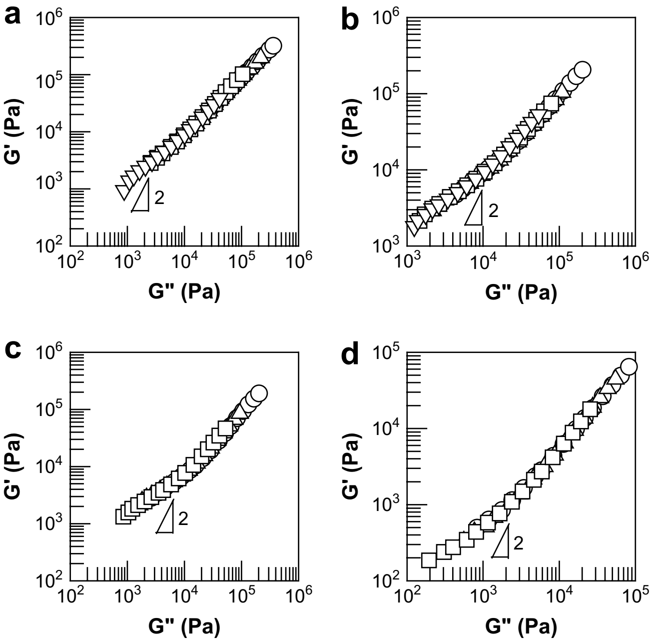


Fig. 12. Plots of log G' versus log G'' for P2VP/HPNBCOOH blends at various temperatures: (a) 20/80 P2VP/HPNBCOOH blend: (○) 98 °C, (△) 108 °C, (□) 118 °C, and (▽) 128 °C; (b) 40/60 P2VP/HPNBCOOH blend: (○) 104 °C, (△) 114 °C, (□) 124 °C, and (▽) 134 °C; (c) 60/40 P2VP/HPNBCOOH blend: (○) 110 °C, (△) 120 °C, and (□) 130 °C; (d) 80/20 P2VP/HPNBCOOH blend: (○) 119 °C, (△) 129 °C, and (□) 139 °C.

Fig. 12 gives log G' versus log G'' plots for 20/80, 40/60, 60/40, and 80/20 P2VP/HPNBCOOH blends at various temperatures. It can be seen in Fig. 12 that the plots are independent of temperature for all four blends over the entire range of temperatures tested, very similar to the observation made for the PC/HPNBCOOH blends in Fig. 10. Notice again in Fig. 12 that the slope of log G' versus log G'' plots in the terminal region is much less than 2 and the plots have curvature especially for the 60/40 and 80/20 P2VP/HPNBCOOH blends, which is attributed to the formation of strong hydrogen bonds between the pyridine group in P2VP and the –COOH groups in HPNBCOOH. From Figs. 11 and 12 we can conclude that TTS is applicable to P2VP/HPNBCOOH blends with hydrogen bonding.

4. Concluding remarks

In this study, we synthesized, via ring-opening polymerization, hydrogenated functional polynorbornene, HPNBCOOH. The purpose of having synthesized the polymer was to investigate the rheology of model miscible polymer blends with hydrogen bonding. We have found that blends of HPNBCOOH with PC or P2VP are miscible on the basis of DSC thermograms exhibiting a single, broad glass transition and the blends form hydrogen bonds over the entire range of blend compositions investigated.

It has been observed experimentally [49–51] that TTS is applicable to miscible polymer blends without specific interaction only when the difference in glass transition temperature (ΔT_g) between the constituent components is about 20 °C or less. It is the general consensus among researchers that concentration fluctuations [52–55] and/or dynamic heterogeneity [53,55–61] cause the failure of TTS in the miscible polymer blends without specific interaction when ΔT_g is larger than about 20 °C. Interestingly, however, in the present study we have found that TTS is applicable to both PC/HPNBCOOH and P2VP/HPNBCOOH blend systems investigated in this study (see Figs. 9–12), in spite of the fact that ΔT_g is 91 °C for the PC/HPNBCOOH blends and ΔT_g is 36 °C for the P2VP/

HPNBCOOH blends. On the basis of our previous study [36], we conclude that hydrogen bonding suppressed concentration fluctuations and dynamic heterogeneity in PC/HPNBCOOH and P2VP/HPNBCOOH blends, warranting the application of TTS to both blend systems.

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