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Soluble graft-like complexes based on poly(4-vinyl pyridine) and carboxy-terminated polystyrene oligomers due to hydrogen bonding

Shiyong Liu, Guangzhao Zhang, Ming Jiang*

Institute of Macromolecular Science and Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, People's Republic of China

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Abstract

Mono-carboxy terminated polystyrene oligomer (MCPS) and di-carboxy terminated polystyrene oligomer (DCPS) were prepared by anionic polymerization. Viscometry and dynamic light scattering (DLS) studies show that both MCPS and DCPS can interact with poly(4-vinyl pyridine) (PVPy) via hydrogen bonding to form soluble graft-like complexes in $CHCl_3$. The marked differences in the viscosity–composition behaviour, intrinsic viscosities and hydrodynamic radius distributions $f(R_h)$ between MCPS/PVPy and DCPS/PVPy blend solutions proved that the two carboxyl ends in DCPS provide much stronger ability for complex formation than the mono carboxyl end in MCPS does.

Keywords: Soluble graft-like complex; LLS; Viscometry

1. Introduction

In recent years, we have systematically studied polymer blends in which the specific interactions, i.e. hydrogen bonding, between component polymers are controllable [1]. It was found that by progressively increasing the density of specific interaction groups introduced into an otherwise immiscible blend, not only miscibility but also interpolymer complexation can be realized [1–11]. In dilute blend solutions, strengthening the interactions will lead to a transition from independent coils to intermolecular complexes. The proton donating polymers employed include styrene-based carboxyl-containing polymers such as carboxylated polystyrene (CPS) and hydroxyl-containing polymers, the proton-accepting polymers employed include pyridyl or carbonyl containing polymers.

It should be noted that in these blend systems, the proton donor or acceptor groups are randomly distributed on the polymer chains. When complexation in solution takes place, the unlike polymer chains tend to combine and aggregate, accompanied by collapse of the chains. Generally, the complex aggregate is ill-defined and often precipitates in solution, thus it causes some difficulties in examining the complexation process and exploring the complex structure. So our present research on interpolymer complexation is targeting at obtaining soluble complexes with relatively well-defined structure.

It was reported [12–14] that end-functionalized oligomers can interact with ionomers via ionic bonding to produce graft-like complexes. The research focused on the phase structure and mechanical properties of the complexes rather than their molecular structure and solution properties.

As far as we know, there have been no experimental reports in the literature about the graft-like complexation between a flexible polymer and end-functionalized oligomer through reversible hydrogen bonding. Our current interest lies in the formation of graft-like complex and their characteristics in solution as well as their phase transition behavior and bulk morphology. A series of end-functionalized oligomers with different end groups, namely, $-C(CF_3)_2OH$, $-CH_2OH$, $-COOH$ and $-N(CH_3)_2$ has been used.

In this communication, we report on mono-carboxy terminated polystyrene (MCPS) and di-carboxy terminated polystyrene (DCPS) as model one-end functionalized oligomers. Graft-like complexes through hydrogen bonding between the oligomers and poly(4-vinyl pyridine) (PVPy) are studied with emphasis on solution properties.

2. Experimental

2.1. Materials

THF, benzene, styrene and 4-vinyl pyridine were purified

* Corresponding author. Tel.: + 86-21-6564-3919; fax: + 86-21-6564-0293.

E-mail address: mjiang@fudan.ac.cn (M. Jiang)

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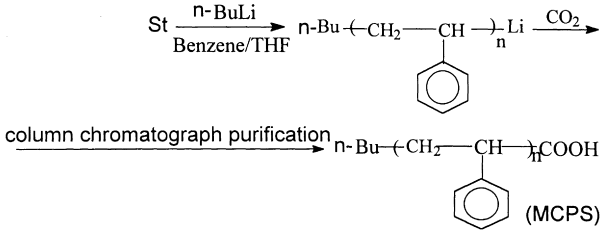


Scheme 1.

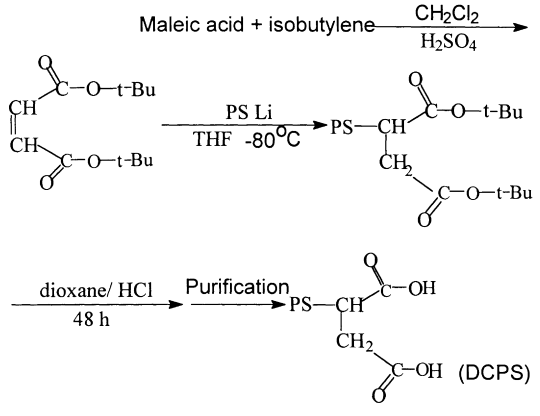
by general methods [16,17]. Maleic acid was analytical grade and used as received.

2.2. Preparation of MCPS (Scheme 1)

Anionic polymerization of styrene was carried out at −20°C in benzene/THF(3/1) using *n*-BuLi in cyclohexane (about 1 M) as the initiator, and the living polystyryl was terminated by CO_2 free of oxygen and protonic impurities. The polymer was precipitated into methanol twice. The crude product was successfully purified by passing through silica gel columns monitored by thin layer chromatography (TLC) using CH_2Cl_2 and ethyl ether as eluents to elute out, in turn, the side product such as polystyrene, $(PS)_2C{=}O$ and $(PS)_3COH$, and the MCPS [18]. The ethyl ether elution was concentrated and precipitated into methanol, the precipitate was then dried under vacuum at 50°C. FTIR of MCPS shows a strong carbonyl stretching peak at 1706 cm^{-1}. ^{13}C-NMR shows a signal of carbonyl at 179 ppm. The functionality of MCPS was found to be 0.98 from the results of SEC and acid–base titration using $NaOCH_3$/toluene.

2.3. Preparation of DCPS (Scheme 2)

For preparing DCPS, instead of using dimethyl maleate as the end capping reagent for the living polystyryl anion as reported in Ref. [15], we used di-*t*-butyl maleate. This change not only reduced the possibility of the attack of polystyryl anion on the ester carbonyl, but also made it possible to conduct the hydrolysis more conveniently in a milder manner. Di-*t*-butyl maleate was prepared from isobutylene and maleic acid [19]. Characterization data for DCPS: ^{1}H NMR ($CDCl_3$): δ6.05 (s, 2H, CH=CH) and 1.51 (s, 18H, *t*-Bu); FTIR: 1720 cm^{-1} and 1632 cm^{-1} ($CDCl_3$). The living PSLi was prepared in THF at −80°C. Di-*t*-butyl maleate (twice the amount of *n*-BuLi used) solution in fresh absolute THF was added by syringe to the polystyryl anion causing its characteristic dark red color to change to light yellow in seconds. Degassed methanol was added to terminate the reaction. The diester-terminated polystyrene was precipitated into methanol twice, filtered, and dried at room temperature under vacuum. FTIR shows ester carbonyl peak at 1727 cm^{-1}.



Scheme 2.

Table 1
Characteristics of the samples[a]

Samples	N	M_n	M_w/M_n	f
MCPS	53	5523	1.06	0.98
DCPS	53	5500	1.25	1.90
PVPy	1330	1.4×10^{5}[b]	—	—

[a] N = average number of units per chain; f = functionality.
[b] Calculated from intrinsic viscosity data.

The diester-terminated polystyrene was hydrolyzed in dioxane and HCl at 80°C for 24 h. Then the polymer was precipitated into methanol twice and dried under vacuum at 50°C for two days. FTIR shows that the ester carbonyl peak at 1727 cm^{-1} disappeared completely, to be replaced by two bands at 1712 and 1742 cm^{-1}, attributable to carbonyl stretching of the hydrogen bonded and free carboxyls, respectively [15]. The functionalities of DCPS was found to be 1.90.

Poly(4-vinyl pyridine) (PVPy) was prepared by anionic polymerization in THF at a concentration of 0.8 mol/l and − 50°C using naphthalene sodium as the initiator. The product was purified in methanol–ethyl ether cycle three times. The molecular weight of PVPy was calculated from intrinsic viscosity ($[\eta]$dl/g) data in absolute ethanol using $[\eta] = 2.5 \times 10^{-2} \times M_\eta^{0.68}$.

2.4. Characterization

FTIR spectra were recorded in $CDCl_3$ on a Nicolet Magna 550. ^{13}C NMR spectra were obtained on a Bruker MSI-300. Viscosity measurements for the solutions in $CHCl_3$ were conducted using an Ubbelohde viscometer at 25 ± 0.05°C. DLS studies of the solutions in $CHCl_3$ were performed on a modified commercial LLS spectrometer (ALV/SP-125) equipped with a multi-τ digital time correlator (ALV-5000) and a solid-state laser (ADLAS DPY 425 II, output power ≅ 400 mW at λ_0 = 532 nm). The molecular weights of MCPS and DCPS were measured by size exclusion chromatography (SEC) using THF as solvent and monodisperse polystyrene samples as calibration standard.

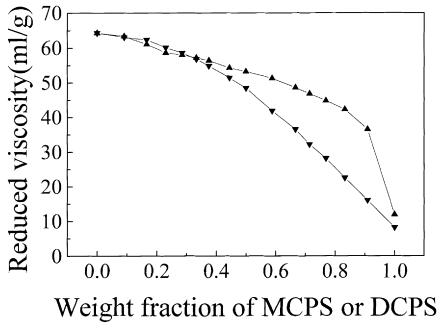


Fig. 1. Reduced viscosity of blend solutions of MCPS/PVPy (▼) and DCPS/PVPy (▲) versus weight composition of MCPS or DCPS in $CHCl_3$ at total concentration of 1×10^{-2} g/ml.

3. Results and discussion

The characterization data of the relevant samples are given in Table 1.

Fig. 1 shows the reduced viscosity of blend solutions of PVPy/MCPS and PVPy/DCPS in $CHCl_3$, which is almost inert to hydrogen bonding, as a function of the blend composition. A total concentration of 1×10^{-2} g/ml was used for the following reason. It is well known that polymer coils are separated if the solution concentration is below its overlap concentration C^*. The C^* estimated by $C^* = 1/[\eta]$ for PVPy in $CHCl_3$ is 1.9×10^{-2} g/ml and well above 0.1 g/ml for MCPS and DCPS. So at the present total concentration of 1×10^{-2} g/ml, if there are no specific interactions between the polymer chains, the chains are expected to remain separated and behave independently and thus the viscosity of the solutions follows the additivity law. This was found to be true for the control, i.e. PVPy/polystyrene (oligomers with the same molecular weight as MCPS and DCPS) blend solutions. In contrast, both the blend solutions of MCPS/PVPy and DCPS/PVPy clearly show a positive deviation from the additivity law. This deviation can obviously be attributed to intermolecular complexation. As the MCPS or DCPS oligomers have proton donor groups at the one chain end only, in the solution, the active end groups attaching to PVPy chain to form graft-like complexes are expected. Moreover, all of the blend solutions remain clear at any composition, so we have got a new type of soluble graft-like complexes via hydrogen bonding as schematically illustrated in Fig. 2. This kind of

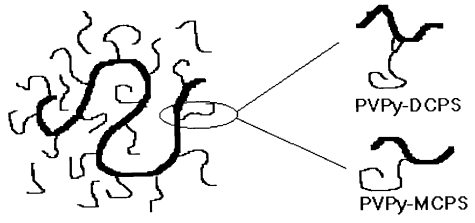


Fig. 2. A schematic illustration of soluble graft-like complexes consisting of PVPy and MCPS or DCPS.

complexation will lead to an increase in hydrodynamic volume relative to the pure components just as shown by the increase in viscosity. This is different from the conventional complexation process where the interaction sites are randomly distributed along the component chains and the complexation is accompanied by chain collapse [1–10]. With respect to the hydrogen bond interactions between the carboxyl end of oligomers and pyridyl, we have got evidence from ^{13}C NMR measurements. In the blend solution of PVPy and MCPS in chloroform, the signal of carboxyl carbon shifts from 179 ppm to high field at 176 ppm on the addition of PVPy which reflects the self-association of carboxyl in MCPS chains is disrupted by the formation of intermolecular hydrogen bonding between carboxy hydroxyl and pyridyl.

It is interesting to note that DCPS/PVPy solutions show much larger positive deviation from the additivity law than MCPS/PVPy, especially for those containing only a small portion of PVPy. For example, addition of 10 wt.% PVPy into DCPS solution leads to a large increase in viscosity from 15 to 40 ml/g, while it only causes a small increase for the MCPS solution. As MCPS and DCPS have the same molecular weight, this difference is reasonably attributed to their difference in the structure of the end groups, i.e. the double carboxyl groups in the chain end of DCPS greatly strengthen its ability to complex with PVPy chains.

Fig. 3 shows the reduced viscosities of blend solutions of MCPS/PVPy(9/1, w/w) and DCPS/PVPy(9/1, w/w) as functions of concentration. Also shown are the data for the pure components. Two facts are noteworthy. First, the reduced viscosity of the blend solutions varies linearly with concentration, which implies that almost no dissociation takes place during dilution. Second, the intrinsic viscosities of both MCPS/PVPy(9/1) and DCPS/PVPy(9/1) are markedly larger than their respective additivity values, indicating the graft-like complexation. The much greater value of the DCPS blend over the MCPS blend indicates a greater ability of DCPS forming the graft-like complexes. The related data are summarized in Table 2.

Fig. 4 depicts the apparent hydrodynamic radius distributions $f(R_h)$ of DCPS, PVPy and their blends with different compositions in $CHCl_3$ at a total concentration of 1×10^{-3} g/ml. DCPS with a narrow molecular weight distribution shows a relatively broad distribution of R_h ranging from around 2 to 10 nm, which may imply the coexistence of the single DCPS chain, its dimers and multimers formed by self-association. Pure DCPS and PVPy show distribution peaks at around 5 and 17 nm, respectively. All the blend solutions investigated show broad R_h distributions and the peak associated with pure DCPS disappears. Generally, the distribution curves move towards larger R_h as the content of DCPS in the blends increases. A remarkable shift of the distribution curve to high values of R_h is observed for DCPS/PVPy (9/1 wt/wt). The peak value reaches 29 nm. In this case, the ratio of the chain number of DCPS to PVPy is as large as 230/1, thus it is reasonable to think

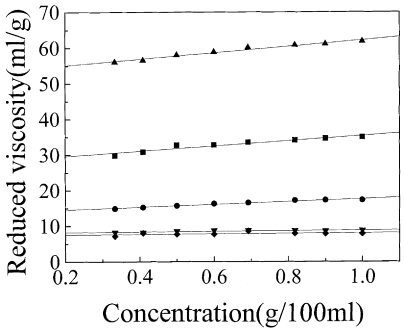


Fig. 3. Reduced viscosity of PVPy (▲), DCPS (▼), MCPS (◆), DCPS/PVPy 9/1 (■) and MCPS/PVPy 9/1 (●) versus concentration in $CHCl_3$.

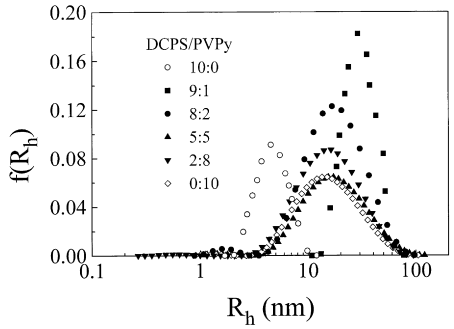


Fig. 4. Hydrodynamic radius distributions $f(R_h)$ of PVPy/DCPS blends with various compositions in $CHCl_3$.

that in forming a complex, PVPy chains may play the role of nuclei and each complex molecule contains one PVPy chain.

From the R_h peak values of PVPy and complex molecules, we are able to make a rough estimation of the composition of the complex molecules. For 9/1 DCPS/PVPy blends, the hydrodynamic volume ratio of the complex molecule to PVPy is calculated to be 4.96. Assuming that the chain density is about the same in pure PVPy and in the complex, and based on the volume ratio and the molecular weight of PVPy, the molecular weight of the complex can be estimated to be 6.95×10^5 and consequently, on average, there is about 101 DCPS chains attached to a PVPy chain.

Similar LLS results were obtained for MCPS/PVPy systems. The blend solution of MCPS/PVPy 9/1 gives a relatively narrow distribution with a peak located at 24 nm. A similar calculation led to the result that, on average, there are about 46 MCPS chains attached to a PVPy chain, which is much less than in the case of DCPS/PVPy. In other words, among 1400 monomer units of each PVPy chain, about 1/7 and 1/30 of the units are connected to DCPS and MCPS, respectively, as one DCPS chain having two interaction sites is considered.

LLS experiments also reveal that dilution of the blend solutions of MCPS/PVPy or DCPS/PVPy has no effect on the R_h distribution, this further confirms the conclusion that the graft-like complexes are very stable on dilution.

Obviously, the grafting density in our polymer/oligomer systems is much lower than that in the polymer/surfactant complexes where almost each monomer unit has its own branch [20]. This is understandable because the steric hindrance of the oligomers with molecular weight around 5000 will make its regularly close packing along the polymer backbone impossible. At the same time, the PVPy chains may undergo chain extension due to the stiffening effect of bound DCPS or MCPS chain, especially in the DCPS case with higher density of bound sites.

Table 2
The intrinsic viscosities (ml/g) of graft-like complexes and pure components

PVPy	MCPS	DCPS	MCPS/PVPy(9/1)		DCPS/PVPy(9/1)	
			Calculated	Measured	Calculated	Measured
55.0	7.4	8.0	12.6	14.8	13.2	29.1

Based on all experimental results, we can conclude that in the blend solutions of PVPy and MCPS or DCPS, interpolymer hydrogen bonding leads to soluble graft-like complexes and the di-carboxyl end of DCPS provides a much stronger ability to form complexes with PVPy than does the mono-carboxyl end of MCPS. The results about the phase transition behavior and morphology of the PVPy/MCPS and PVPy/DCPS blends in bulk will be reported in our forthcoming articles.

Acknowledgements

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