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STUDY OF POLY(2-VINYL PYRIDINE)-POLY(METHYL METHACRYLATE) GRAFT COPOLYMERS IN SELECTIVE SOLVENTS: MICELLE FORMATION

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Abstract—A graft copolymer consisting of a poly(2-vinyl pyridine) backbone chain and of poly(methyl methacrylate) side chains, prepared anionically, has been studied in dilute solution, in selective solvents, using viscometric and light scattering techniques. In some solvent media in which the backbone chain is insoluble the copolymers remain soluble due to a "protective" effect of the side chains. In this solvent media the copolymer is found either as monomolecular or polymolecular micelles.

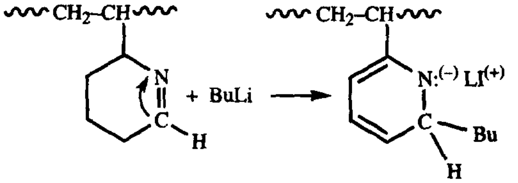
INTRODUCTION

Much work has been directed to the study of copolymers in solution. A major part of this work has been concerned with the special conformation of graft and block copolymers in selective solvents. The micellization of these copolymers in selective solvents is their most characteristic property [1–4].

In this article we study a graft copolymer prepared according to an 'old' anionic method [5] based on the formation of side chains of poly(methyl methacrylate) on active sites existing on a poly(2-vinyl pyridine) chain. This study is based essentially on the existence of selective solvents for this copolymer. In these solvents micellization occurs with this graft copolymer. This phenomenon will be examined by light scattering and viscometry varying the composition of the mixture of a common and a selective solvent at a given temperature, as well as the temperature when the polymer is found in a selective solvent.

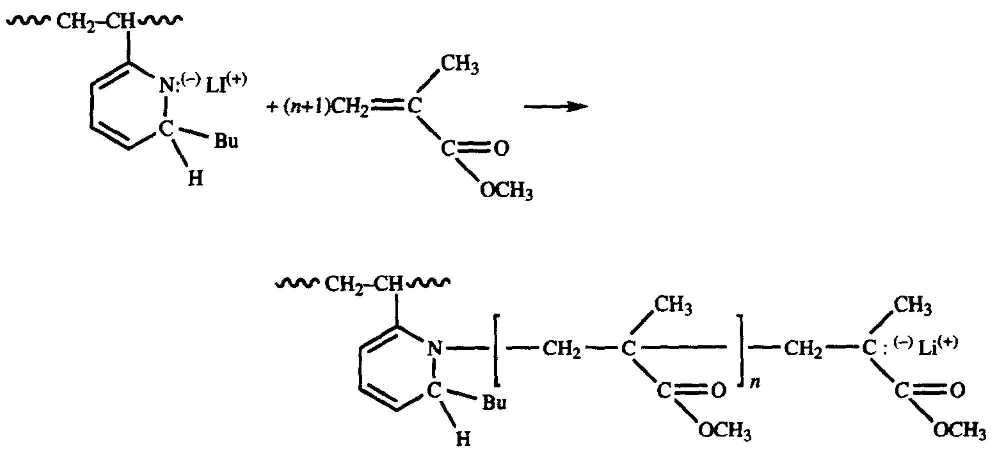
EXPERIMENTAL

The graft copolymers used in this work were prepared in the Institute "Charles Sadron" in Strasbourg. The synthetic procedure [5] consists of two steps. In a first step metallation of the poly(2-vinyl pyridine) (P2VP) chain with a molecular mass equal to 112,000 takes place according to the reaction (Scheme 1).



Scheme 1

In the second step, (Scheme 2) the formed anionic active sights initiate the polymerization of the methyl methacrylate leading to the formation of poly(methyl methacrylate) (PMMA) side chains



Scheme 2

The grafting frequency corresponds to the percentage of metallation (percentage of the P2VP monomeric units

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Table 1. Calculated and determined molecular masses (in pure THF), percentage of the backbone metallation and P2VP contents (w/w) of three P2VP–PMMA graft copolymers

Sample	$M_{w_{calc}}$	$M_{w_{det}}$	Metallation (%)	P2VP (%)
A	794,000	860,000	6	14
B	1,025,000	1,700,000	20	8
C	710,000	740,000	5	12

that have been attacked by the BuLi). There is no reason to have a synergetic effect and we believe that the metallation (formation of active sites) and consequently the side chains are randomly created on the backbone.

In Table 1 we give the percentage of the metallation of the backbone (P2VP) chain, the percentage of this chain (w/w) in the copolymer and the calculated and determined molecular mass of the P2VP–PMMA copolymers. The calculated or 'expected' molecular mass of the copolymers can be obtained approximately from the amount of the final product. Since the yield of the reaction was always about 95–97% (w/w) we assume that all of the added MMA was polymerized. As we can see in this table the determined molecular mass of the copolymers is very close to the calculated values and this indicates that the side reactions (reticulation of the P2VP chains [5]) are almost non-existent. The polydispersity of the copolymers lies near a value of 2. According to the preparation procedure no PMMA homopolymer must be formed.

The light scattering measurements have been performed in a FICA photogoniodifusiometer apparatus and the viscosity measurements using an automatic viscometer. The intrinsic viscosities, [η], are measured at 20°C and they are given in ml/g.

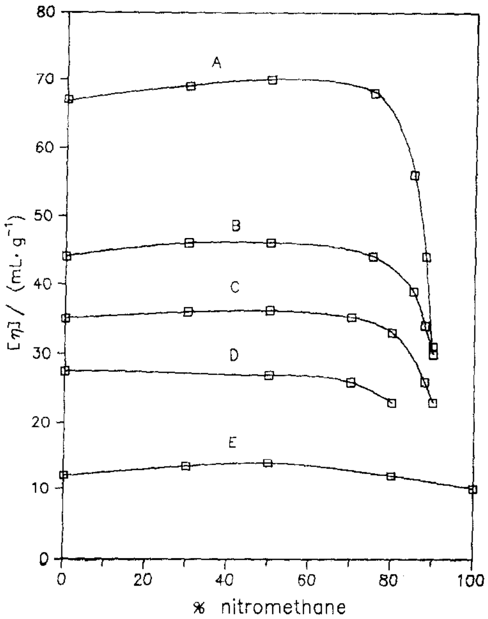

Fig. 1. Plots of intrinsic viscosity vs the binary solvent mixture (THF–nitromethane) composition expressed by the volume fraction of nitromethane. Curves A, B and C were obtained with A, B and C copolymers of Table 1. Curve D was obtained with a P2VP homopolymer ($M_W = 112{,}000$), curve E was obtained with a PMMA homopolymer ($M_W = 29{,}000$).

RESULTS AND DISCUSSION

Variation of the quality of the solvent at constant temperature

We started the viscometric study of the P2VP–PMMA copolymers in the tetrahydrofuran–nitromethane (THF–CH_3NO_2) solvent mixture (expressed by v/v) at a constant temperature of 20°C. In Fig. 1 we present the variation of the intrinsic viscosity, [η], as a function of the solvent mixture composition. THF is a good solvent for both components of the copolymers while nitromethane is a precipitant for the backbone (P2VP) of the copolymer. Curves A, B and C are obtained with copolymers A, B and C of Table 1, curve D is obtained with P2VP homopolymer of molecular mass equal to 112,000 and curve E is obtained with a PMMA homopolymer of molecular mass equal to 29,000. As was expected, P2VP homopolymer is not soluble in solvent mixtures containing an important percentage of nitromethane (precipitation above 89% in nitromethane). PMMA, on the contrary, is soluble over the entire composition of the solvent mixture.

The intrinsic viscosity of the copolymers strongly decreases when the mixture contains more than 80% nitromethane. This decrease can be attributed to the formation of monomolecular or polymolecular micelles due to the precipitation of the backbone of the copolymers. Nevertheless, we have only monomolecular micelles because the light scattering measurements show that copolymers present the same molecular weight in the pure THF and in the mixture containing 90% nitromethane. More precisely copolymers A and B in pure THF produce molecular masses 860,000 and 1,700,000 respectively, in the mixture containing 90% nitromethane they produce molecular masses 880,000 and 1,800,000 respectively. One can present an objection on the determination of the molecular mass of the copolymers in the solvent mixture. The obtained molecular mass is generally an apparent molecular mass, M^* [6]. More precisely, the apparent molecular mass M^*, is related to the true molecular mass, M, by the relation proposed by Strazielle and Benoit [7]

$$M^* = M\left[1 + \lambda_1'\left(\frac{dn_0}{d\Phi_1}\Big/\frac{dn}{dc}\right)\right]^2$$

where dn/dc is the refractive index increment of the polymer in the solvent mixture, $dn_0/d\Phi_1$ is the refractive index increment of the binary solvent mixture with respect to one of the solvents and λ_1' is the preferential sorption coefficient. The quantity $dn_0/d\Phi_1$ lies very near to the difference n_1–n_2 of the refractive indices of the two solvents. In the case of THF (solvent 1)-nitromethane (solvent 2) used here, n_1–n_2 is extremely low (0.018). Nevertheless, the obtained slightly higher values of molecular masses of the copolymers in the mixture THF + 90% nitromethane, indicate that THF is preferentially adsorbed by the copolymers.

When the copolymers are dissolved in pure THF their molecular masses can be considered as true values because the fractionation of these copolymers has shown that all the fractions have about the same chemical composition; these results are already presented in Ref. [5].

In Fig. 2 we give the variation of the radius of gyration of copolymers A and B (curves A and B) with the solvent mixture composition and we also

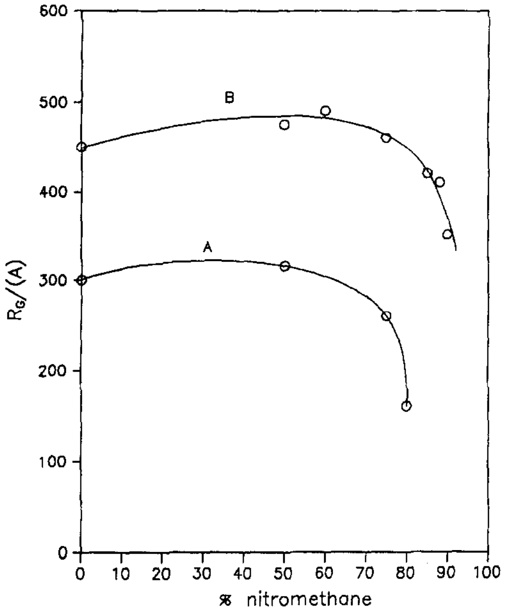

Fig. 2. Plots of radius of gyration vs the binary solvent mixture (THF–nitromethane) composition expressed by the volume fraction of nitromethane. Curves A and B correspond to the copolymers A and B of Table 1.

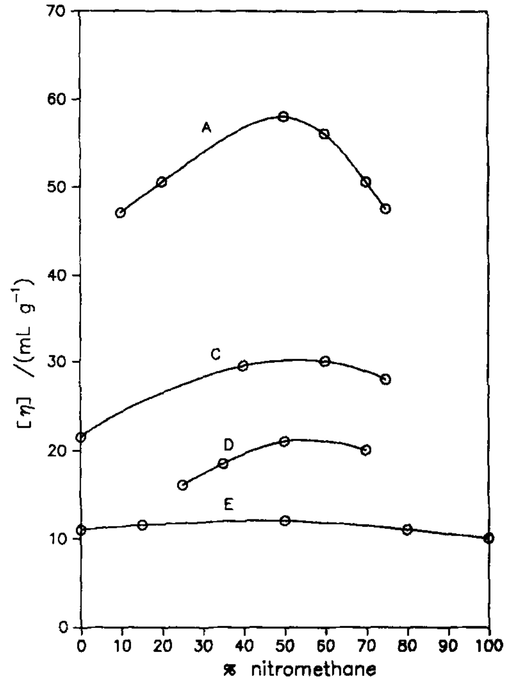

Fig. 3. Plots of intrinsic viscosity vs the binary solvent mixture (ethyl acetate–nitromethane) composition expressed by the volume fraction of nitromethane at 20°C. Curve D was obtained with a P2VP homopolymer ($M_W = 112{,}000$). Curve E was obtained with a PMMA homopolymer ($M_W = 29{,}000$). Curve A was obtained with the copolymer A and curve C obtained with the copolymer C (Table 1).

observe a sharp decrease of this radius of gyration when we are in a solvent mixture in which the backbone of the copolymers (P2VP) is precipitated. It is known [8] that the radius of gyration of graft copolymers is generally apparent as it depends on the refractive index of the solvent. Nevertheless, the two solvents used here, as we have already mentioned, have almost identical values of refractive indices. For this reason, the observed decrease of the radius of gyration in Fig. 2 cannot be attributed to the variation of the composition of the solvents.

Let us indicate that copolymer A presents a higher value of intrinsic viscosity than copolymer B (Fig. 1) while its molecular mass is lower (Table 1). This must be attributed to a less compact structure of copolymer A due to the preparation procedure (6% metallation for copolymer A and 20% metallation for copolymer B).

All the curves of Figs 1 and 2 present an upwards curvature and this must be attributed to a repulsion between the molecules of nitromethane and THF. A possible positive free enthalpy of mixing of these solvents ($\Delta G > 0$) must have caused the upward curvature of the curves of Figs 1 and 2, as was already observed for many other systems [9–12].

Going from the pure THF to the mixture containing 90% nitromethane, in which the copolymers must exhibit a segregated form (precipitation of the backbone chain) we do not observe any transition phenomena because at 20°C these copolymers in pure THF present also a rather segregated conformation [13].

Ethyl acetate is a precipitant for P2VP like nitromethane. In mixtures of these two non-solvents this polymer is soluble (co-solvency phenomenon) and more precisely the P2VP fraction of molecular mass equal to 112,000 is soluble in solvent mixtures containing 25–70% nitromethane. The curve D of Fig. 3 represents the variation of the intrinsic viscosity of this P2VP fraction in the solvent mixture region in which P2VP remains soluble. On both sides of this solvent mixture region as well as in the two pure solvents P2VP is not soluble. PMMA on the contrary is soluble in both solvents and the variation of $[\eta]$ of a fraction of this polymer is also presented in Fig. 3 (curve E). Copolymer A of Table 1 (curve A) presents a real co-solvency effect (insoluble in both pure solvents) but the solubility region is more expanded than the region of P2VP. The copolymer C of Table 1 ($M_W = 740{,}000$) is soluble in pure ethyl acetate and remains soluble up to a mixture containing 75% nitromethane (curve C). Comparison of curves A and C with curve D clearly indicates the 'protecting' effect of the PMMA side chains to the P2VP backbone that makes the copolymer soluble in a solvent or solvent mixtures in which the backbone chain is itself insoluble.

Variation of the quality of the solvent with temperature

The copolymer P2VP–PMMA A in pure nitromethane at 20°C is not found in monomolecular dispersion as is shown in Fig. 4. This curve is characteristic of a system that forms polymolecular clusters. It is known that η_i/c is proportional to the ratio V/M where V is the hydrodynamic volume of the polymer and M its molecular mass. The decrease of η_i/c with increasing concentration indicates that the increase of the molecular mass is faster than the increase of the hydrodynamic volume during the

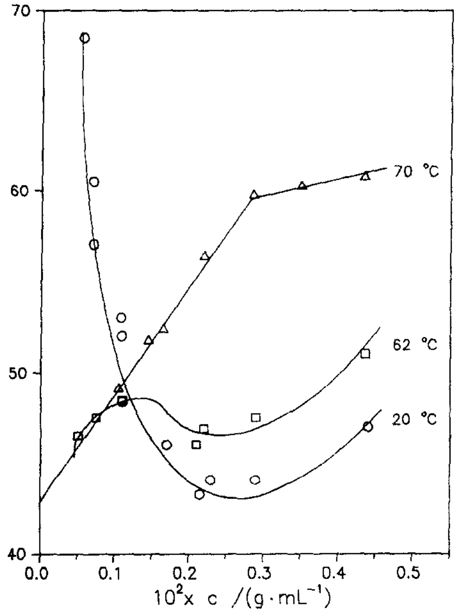

Fig. 4. Plots of the reduced viscosity of copolymer A of Table 1 vs the concentration in pure nitromethane in three different temperatures.

formation of polymolecular clusters or in other words these clusters become more and more compact as the number of the molecules from which they consist, becomes more and more higher. Nevertheless the system is not precipitated because of the 'protecting' effect of the PMMA part of the copolymer. In 62°C the same copolymer in pure nitromethane presents an incipient desegregation in the region of very low concentrations (Fig. 4). The same copolymer in 70°C presents a 'normal' behaviour in the variation of η_i/c as a function of c, in the concentration region up to 0.26 g/100 mol (Fig. 4). The extrapolation of the curve obtained in this concentration region to $c = 0$ gives a very low value of the intrinsic viscosity of this copolymer ($[\eta] = 43$ ml/g). The $[\eta]$ value of this copolymer in pure THF (good solvent for both parts of the copolymer) is equal to 67 ml/g.

CONCLUSIONS

This study of graft copolymers P2VP–PMMA, by viscometry and light scattering, demonstrates that the PMMA side chains provoke a solubility of the copolymers, in solvent media in which the backbone itself is precipitated. In this media the molecular dimensions of the copolymers are lower than in Θ conditions. It is known that the unperturbed dimensions of PMMA, that is the main part of the copolymer (around 85%, Table 1) as they are expressed by the parameter K_Θ ($K_\Theta = [\eta]_\Theta/M^{1/2}$) lie near a mean value of 5.1×10^{-2} ml/g$^{-3/2}$ mol$^{1/2}$. Copolymers A, B and C in the THF–nitromethane mixture containing 90% nitromethane (Fig. 1) have intrinsic viscosities equal to 31. 7, 30 and 23 respectively. Dividing these values by the mean square of the molecular mass of the corresponding copolymer we obtain the values 3.4×10^{-2}, 2.3×10^{-2} and 2.7×10^{-2}. These values are lower than the value of K_Θ of PMMA and P2VP (5.1×10^{-2} and 8×10^{-2} respectively) indicating that these copolymers in this media exhibit a conformation of very high segment density due to the collapsed P2VP backbone inside the monomolecular micelles.

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