

Poly(*p*-phenyleneterephthalamide)-Based Nanocomposites Obtained by Matrix Polycondensation. Synthesis and Solid-State NMR Characterization

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ABSTRACT: Matrix polymerization can be viewed as an intriguing procedure for the preparation of homogeneous blends that are otherwise difficult or practically impossible to prepare. Poly(*p*-phenyleneterephthalamide) has been synthesized by direct polycondensation in the presence of poly(*N*-vinylpyrrolidone) or poly(4-vinylpyridine) as polymer matrices. The molecular weight effect of the latter polymers on the intrinsic viscosity of the aramid has been investigated. Poly(*p*-phenyleneterephthalamide), characterized by intrinsic viscosity as high as 14.2 dL/g, is obtained when high molecular weight poly(*N*-vinylpyrrolidone) is used. The intimate composites formed in situ have been characterized by solid-state NMR. The parent and daughter polymers in the composite present the same proton T_1 relaxation times in the rotating frame, and this value differs from that of the neat polymers; this result demonstrates the intimacy of the blend at the level of a few nanometers.

Introduction

Template polymerization is a well-known synthetic approach, based mainly on chain polyaddition, and has been comprehensively described in recent years.^{1,2} This synthetic route is based on a macromolecular synthesis, in which a polymer is obtained in the presence of a second macromolecular compound able to govern the growth of the first. The influence exerted by the templating (*parent*) polymer on the growing (*daughter*) macromolecule is generally called "the template effect". This approach mimics the known examples in nature, such as the self-replication of DNA. In general, enhanced rates as well as high selectivity and efficiency characterize template reactions in the biological field. As a consequence, both the molecular weight and the sequence of repeat units are strictly predetermined. When template polymerization is carried out in non-biological systems, control of the polymerization process is less effective, and polydispersed macromolecular compounds are usually synthesized. However, also in this case an enhancement of the polymerization rate is obtained, and it is possible to determine the molecular weight and the microstructure of the daughter polymer by carefully choosing the parent polymer.^{1,2}

Template polymerization using stepwise polycondensation, best known as *matrix polycondensation*, has been found to be a useful method for the preparation of homogeneous macromolecular composites.³ The resultant material is characterized by enhanced mechanical properties. Furthermore, with matrix polymerization the incompatibility of polymer–inorganic compound pairs in hybrid composites can be easily overcome,⁴ thus

making it possible to obtain materials otherwise difficult to be produced.

Aromatic polyamides (aramids) are industrially synthesized using the reaction between the chlorides of aromatic dicarboxylic acids and aromatic diamines (*indirect* synthesis). The aramids obtained by this route are endowed with high molecular weights. Still, the difficulty to synthesize, purify, and store acyl chlorides makes the above approach not completely free of handling problems. An alternative way to synthesize aromatic polyamides in quantitative yields exploits the *direct* synthesis from the corresponding acids.^{5–11} However, the molecular weights of the resultant aramids are generally lower than those typical of indirect synthesis. To overcome this drawback, the effect of several polymer matrices in matrix polycondensation has been studied. In particular, poly(4-vinylpyridine) (P4VP),^{12,13} poly(ethylene oxide),¹⁴ and poly(vinylpyrrolidone) (PVP)^{13,15} have been successfully used. The above polymers are able to exert many simultaneous effects on the overall polymerization kinetics. One effect is that they increase the local concentration of the monomers and the reactivity of functional groups. Indeed, the inherent viscosity of the resulting aramids has been found to be much higher, even more than twice that observed in the case of a blank preparation.

Here we report the characterization of poly(*p*-phenyleneterephthalamide) (PPDT) dispersed in P4VP or PVP as obtained by matrix polycondensation. As the main characterization technique, we used solid-state NMR, which has been shown to be a powerful tool for detecting miscibility between two polymers at different dimensional levels. ¹³C chemical shifts in magic angle spinning (MAS) spectra are sensitive to the local environment (a few angstroms) of the carbon atom; conformational changes and intermolecular hydrogen bonding between the blend components are easily detected. Moreover,

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proton relaxation times in solid polymers are not local properties of a group of atoms (proton of CH₂ or CH₃ groups) because the magnetization propagation through ¹H–¹H dipolar interaction (spin-diffusion) can average the local differences. Therefore, the measurement of proton *T*₁ and *T*_{1ρ} relaxation times can be used to establish the length scale over which the blend is homogeneously mixed.¹⁶

Experimental Section

Synthesis. (a) *Materials.* *N*-Methylpyrrolidone (NMP), Aldrich, was refluxed under reduced pressure in the presence of CaH₂ for 8 h and distilled under the same conditions. Then, it was refluxed under reduced pressure in the presence of P₂O₅ for 6 h and distilled; the treatment was repeated twice. Pyridine (Py), Aldrich, was refluxed under inert atmosphere in the presence of NaOH for 6 h and distilled; the treatment was repeated three times. LiCl (Carlo Erba) and CaCl₂ (Fluka) were dried for 24 h at 340 °C under vacuum. Triphenyl phosphite (TPP), Aldrich, was purified by fractional distillation under reduced pressure three times. *p*-Phenylenediamine (PPD), Fluka, was purified by sublimation at reduced pressure three times. Terephthalic acid (TA), Amoco, was dried under vacuum at 80 °C for 24 h. Terephthaloyl chloride (TCl), Aldrich, was purified by sublimation at reduced pressure three times. P4VP and PVP, Aldrich, were dried under vacuum at 60 °C for 24 h.

(b) *Synthetic Procedures. Direct Synthesis of Low Molecular Weight PPDT in the Presence of P4VP (Yamazaki's Conditions⁵): L Samples.* Operating in a drybox under inert atmosphere, 9 mL of NMP, 6 mL of Py, 0.3068 g of TA, 0.997 g of PPD, 0.39 g of P4VP, 1.11 mL of TPP, and 0.4 g of LiCl were added to a 50 mL three-neck flask, fitted with an inlet and outlet for inert gas (argon) and a magnetic stirrer. Any traces of oxygen in the above-mentioned components had been first removed by several cycles of vacuum and argon. The vessel, with the components, was placed in a thermostatically controlled oil bath at 100 °C, and after 4 h the obtained polymer was ground in a blender in the presence of methanol. The reaction product was washed with boiling methanol and dried in a vacuum oven at 80 °C for 18 h.

Direct Synthesis of High Molecular Weight PPDT in the Presence of P4VP or PVP (Modified Higashi's Conditions¹¹): H Samples. As reported in refs 7–13, a relevant improvement in terms of [η] of PPDT can be obtained by adding CaCl₂ to the above reaction mixture; this salt, mixed with LiCl, strongly enhances the solubility of aramid, allowing higher molecular weights to be reached.

12.5 mL of NMP, 2.5 mL of Py, 0.21 g of TA, 0.13 g of PPD, 0.26 g of P4VP or 0.28 g of PVP, 0.8 mL of TPP, 0.25 g of LiCl, and 1.5 g of CaCl₂ were added to the above reaction vessel set at 115 °C. The polymerization procedure and the operations on the resultant polymer were as mentioned above. However, in this case the reaction was carried out in a gelled medium, and unlike the previous synthetic route, no precipitation was observed.

Indirect Synthesis of High Molecular Weight PPDT in the Presence of PVP: I Samples. By operating in a drybox under inert atmosphere, 16.3 mL of NMP, 1.25 g of CaCl₂, 0.9329 g of PPD, and 1.98 g of PVP were added to a 50 mL three-neck flask, fitted with an inlet and outlet for inert gas (argon) and an efficient mechanical stirrer. Oxygen traces were preliminarily removed from the components mentioned above by several cycles of vacuum and argon. The vessel was placed in a thermostatically controlled bath at 5 °C, and after the complete dissolution of all the above components, 1.7672 g of TCl was added stepwise. The reaction mixture was allowed to react in these conditions for a further 15 min. The polymer obtained was then ground in a blender in the presence of methanol. The reaction product was washed with boiling methanol and dried in a vacuum oven at 80 °C for 18 h.

Viscometry. Viscosity measurements of the polymer solutions (at concentrations ranging between 0.10 and 0.50 g/dL)

were determined in 96% H₂SO₄ at 25 °C using a Ubbelohde-type viscometer.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) traces were performed on a Mettler Toledo Star thermal analysis system. The experiments were run under a nitrogen atmosphere, and the samples were first heated to 190 °C and held for 5 min in order to cancel any thermal history. Then they were cooled to 25 °C at a rate of 40 °C/min. The measuring scans started from this temperature up to 240 °C at a heating rate of 20 °C/min.

Transmission Electron Microscopy. The morphology of the samples was examined by transmission electron microscopy (TEM). The powder was embedded in an epoxy resin and cut by a cryo-microtome LEIKA-ULTACUT R/FCS at –100 °C; the thickness of the slices ranged between 50 and 60 nm. To enhance electron density contrast, the thin films were stained at ambient temperature by ruthenium tetroxide vapors (0.5% w/v aqueous solution) for 1 h. The measurements were carried out on a JEOL JEM 2010 transmission electron microscope. Standard conditions were 200 kV of accelerating voltage.

Solid-State NMR. High-resolution ¹³C MAS NMR spectra were run at 75.5 MHz on a MSL300 Bruker instrument operating at a static field of 7.04 T. A MAS Bruker probe was used with 7 mm ZrO₂ rotors, and the spinning speed was set to 5.5 kHz. The experiments were made using a high-power proton decoupling (DD). The ¹³C cross-polarization MAS (CP-MAS) experiments were performed using a 90° pulse of 4.5 μs with a delay time of 10 s and a contact time of 1 ms (proton decoupling field of 55 kHz). Experiments were run collecting 1000–10000 scans.

Proton relaxation times in the rotating frame *T*_{1ρ}(¹H) were measured indirectly by varying the duration of a ¹H spin-lock period before a fixed ¹H → ¹³C cross-polarization contact period.¹⁷ For each relaxation measurement, 13 spectra were run. The *T*_{1ρ}(¹H) values were calculated using a nonlinear least-squares fitting routine.

The resolution for carbon was checked on glycine (width at half-height = 22 Hz). Crystalline polyethylene (PE) was taken as an external reference at 32.85 ppm from tetramethylsilane (TMS).¹⁸

Results and Discussion

Viscometry and DSC Results. PPDT blends have been obtained using three different synthetic routes: (a) direct synthesis of low molecular weight PPDT in the presence of P4VP, *L samples*; (b) direct synthesis of high molecular weight PPDT in the presence of P4VP or PVP, *H samples*; (c) indirect synthesis of high molecular weight PPDT in the presence of PVP, *I samples*. A complete separation of the daughter aramid from the polymer matrix could not be achieved for all samples. Indeed, it was always found that a relevant, and sometimes very large, amount of the polymer matrix could not be removed from the aramid, neither by solvent extraction of the matrix^{12,14,15} nor by aramid dissolution and reprecipitation. As it was not possible to measure the intrinsic viscosity of the neat aramid, the intrinsic viscosity of the synthetic mixture (parent/daughter pair) ([η]_{composite}) was measured. The intrinsic viscosity values of PPDT were calculated applying the additivity rule generally used for polymer blends in which no strong interaction between the components occurs:

$$[\eta]_{\text{composite}} \cong w_{\text{PPDT}}[\eta]_{\text{PPDT}} + w_{\text{matrix}}[\eta]_{\text{matrix}} \quad (1)$$

where *w*_{PPDT} and *w*_{matrix} are the corresponding weight fractions of PPDT and the matrix, respectively.

To ascertain the applicability of the additivity rule expressed by eq 1, to our system, several PPDT/PVP

Table 1. Comparison between Experimental and Calculated $[\eta]_{\text{mixture}}$ Values of PPDT–PVP Mechanical Mixtures

sample	$[\eta]_{\text{mixture}}^{\text{exptl}}$ (dL/g) ^a	$[\eta]_{\text{mixture}}^{\text{calcd}}$ (dL/g) ^a
PPDT-1	11.00	
PVP-1	0.20	
PVP-2	0.31	
PVP-3	0.42	
PVP-4	2.02	
PPDT-1 + PVP-1 ^c	5.94	6.25
PPDT-1 + PVP-2 ^c	6.12	6.30
PPDT-1 + PVP-3 ^c	6.12	6.35
PPDT-1 + PVP-4 ^c	6.91	7.05

^a In 96% sulfuric acid at 25 °C. ^b On the basis of eq 1. ^c Composition of the mechanical mixture: PPDT/PVP = 0.56/0.44 weight ratio.

Table 2. Intrinsic Viscosity of Low Molecular Weight PPDT, L Samples, Obtained in the Presence of P4VP Samples of Various Molecular Weights, and the Corresponding Blank Sample (Direct Polycondensation, Yamazaki's Method)

sample code	P4VP MW	$[\eta]_{\text{P4VP}}^a$ (dL/g)	$[\eta]_{\text{composite}}^a$ (dL/g)	$[\eta]_{\text{PPDT}}^a$ (dL/g)
PPDT-7				0.22
L-8	10 000	0.64	0.68	0.57 ^b
L-9	16 000	0.74	0.84	0.74 ^b
L-10	27 000	0.78	0.89	0.79 ^b
L-11	260 000	0.92	1.04	0.91 ^b
L-12	400 000	2.04	1.60	0.84 ^b

^a In 96% sulfuric acid at 25 °C. ^b Calculated on the basis of eq 1.

mechanical mixtures have been prepared using samples of PPDT and PVP of known $[\eta]$. The results are given in Table 1. It can be seen that experimental and calculated intrinsic viscosities of the polymer mixtures are always in good agreement (discrepancies within 2–5%). Therefore, strong molecular interactions between the two polymers can be ruled out. Of course, interactions might somehow be present in our in situ blends, and eq 1 may not give an exact evaluation of $[\eta]_{\text{PPDT}}$. At present, however, the real extent of these deviations from the ideality, expressed by eq 1, cannot be estimated. Consequently, eq 1 has been adopted as a reasonable first approximation for the evaluation of $[\eta]_{\text{PPDT}}$. The same assumption has also been made by Henze et al.¹⁹ for the mixture poly(*p*-benzamide)/PVP where, too, it was difficult to separate the two components.

On these grounds, the $[\eta]_{\text{PPDT}}$ data of low MW PPDT, synthesized as mentioned in the Experimental Section by direct polycondensation in the presence of P4VP, using Yamazaki's conditions, are given in Table 2 as functions of the molecular weight of the matrix polymer. All aramids show intrinsic viscosities higher than those of the corresponding blank samples. Namely, the higher the MW of P4VP, the higher is $[\eta]_{\text{PPDT}}$. Intrinsic viscosity data of high molecular weight PPDT, *H samples*, obtained by direct synthesis in the presence of PVP as a polymer matrix using modified Higashi's conditions, are shown in Table 3. The influence of the MW of PVP on the MW of PPDT is clearly evident; in fact, as the MW weight of the parent polymer increases, the MW of daughter polymer increases, too. Indeed, $[\eta]_{\text{PPDT}} = 14.2$ dL/g is one of the highest values obtained for PPDT synthesized by any synthetic route. This value is significantly higher than that of the blank sample and about twice that of the corresponding commercial prod-

Table 3. Intrinsic Viscosity of High Molecular Weight PPDT, H Samples, Obtained in the Presence of PVP of Various MWs, and the Corresponding Blank Sample (Direct Polycondensation Modified Higashi's Method)

sample code	PVP MW	$[\eta]_{\text{PVP}}^a$ (dL/g)	$[\eta]_{\text{composite}}^a$ (dL/g)	$[\eta]_{\text{PPDT}}^a$ (dL/g)
PPDT-1				11.0
H-10	10 000	0.20	2.9	5.4 ^b
H-20	25 000	0.31	3.0	5.5 ^b
H-30	40 000	0.42	3.1	5.6 ^b
H-90	360 000	2.02	8.31	14.2 ^b

^a In 96% sulfuric acid at 25 °C. ^b Calculated on the basis of eq 1.

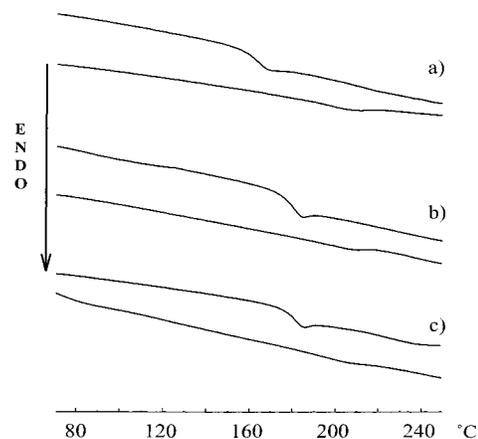


Figure 1. DSC traces: (a) PVP-3, MW = 40 000 (upper trace) and H-30, PPDT/PVP composite obtained by matrix polycondensation using direct synthesis (lower trace); (b) PVP-4, MW = 360 000 (upper trace) and H-90, PPDT/PVP composite obtained by matrix polycondensation using direct synthesis (lower trace); (c) PVP-5, MW = 750 000 (upper trace) and I-1, PPDT/PVP composite obtained by matrix polycondensation using indirect synthesis (lower trace).

ucts (Kevlar, Twaron). The relatively low $[\eta]_{\text{PPDT}}$ values (5.4–5.6 dL/g), obtained when PPDT is synthesized in the presence of low molecular weight PVP, confirm the strong effect exerted by the matrix polymer on the daughter macromolecule, even lowering the MW of the latter. Another example of this relevant influence is given by the direct synthesis of high molecular weight PPDT in the presence of P4VP using modified Higashi's conditions. PPDT with $[\eta]_{\text{PPDT}} = 7.3$ dL/g was obtained with a P4VP matrix having MW of 400 000; the above value of the intrinsic viscosity is considerably lower than that of the corresponding blank sample ($[\eta]_{\text{PPDT}} = 11.0$ dL/g), thus highlighting the complex role of the matrix polymer nature.

DSC measurements were performed for a first evaluation of the degree of mixing of the components in the in situ composite. PPDT shows no thermal transition between 80 and 250 °C,²⁰ whereas PVP shows a glass transition temperature between 160 and 180 °C as a function of its molecular weight.²¹ In Figure 1, the calorimetric curves for some PVP/PPDT in situ composites obtained by direct matrix polymerization are represented together with the curves of the neat parent polymers. In the in situ composites the glass transition of PVP is always quite faint and is shifted to higher temperatures, 40–50 °C higher than that of the neat polymer. As is well-known, in the case of a homogeneous blend constituted of two polymers, both showing glass transitions, the T_g of the blend is in between the values of the neat polymers. In our system, PPDT is a rigid-rod-like polymer with very limited conformational free-

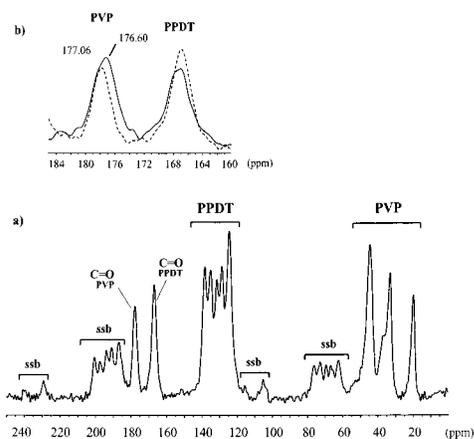


Figure 2. (a) 75.5 MHz ^{13}C CP MAS spectrum of a PPDT and PVP macroscopically mixed (spinning speed of 5500 Hz, contact time of 1 ms). (b) 75.5 MHz ^{13}C CPMAS spectrum of the carbonyl region of H-90, the PPDT/PVP composite obtained by matrix polymerization using direct synthesis (solid line); spectrum of the same region of PPDT and PVP macroscopically mixed (dashed line).

dom and does not present a measurable glass transition. However, in the case of an intimate blend, the stiffness of PPDT will affect the flexible chain of PVP, acting as a constraint to the motion of the latter polymer. The 50 °C increase of PVP T_g can be explained by this reduced mobility; analogous behavior has been reported for cellulose/PVP blends.²¹

To observe phase separation of the polymers, thin sections of our in situ composites have been studied by TEM. Micrographs do not show any phase separation down to ca. 10 nm and are in agreement with solid-state NMR results discussed below. Anyway, the difficulty of obtaining adequately contrasted domains pertaining to the two polymers somehow limits the strength of TEM results. RuO₄ can stain both PPDT and PVP, and a careful choice of the experimental conditions able to improve differences in the staining level is under study.²²

Solid-State NMR Characterization. The ^{13}C CP-MAS spectrum of a sample obtained by filling a rotor with small fragments of a PPDT–PVP mechanical mixture is depicted in Figure 2a. This spectrum represents the simple sum of the spectra of the two neat polymers. The PPDT signals present no overlapping with those of PVP, one polymer being completely aromatic (signals between 140 and 110 ppm)²³ and the other fully aliphatic (three signals at 55, 35, and 20 ppm).²⁴ Also, the two carbonyl carbons, lactamic and amidic ones ($\text{C}=\text{O}_{\text{PVP}}$, 177.1 ppm; $\text{C}=\text{O}_{\text{PPDT}}$, 166.3 ppm), are well separated. Spinning speed was carefully set in order to avoid the overlapping of the spinning sidebands of the PPDT signals with the signals of PVP.

^{13}C CPMAS spectra of several composites, *H* samples, obtained by direct synthesis have been compared to the spectrum of Figure 2a, and no major changes are evident. The PPDT signals show the same CS as the neat polymer. Indeed, this result was expected, considering the very limited conformational freedom of the aramid. Also, the aliphatic peaks of PVP in the synthetic composite show the same CS as in the neat polymers. On the other hand, the resonance due to PVP carbonyl carbon shows a highfield shift of about half ppm going from the neat polymer to the synthetic composite (Figure 2b). Furthermore, a clear increase in the line width is present (pure PVP $\text{C}=\text{O}_{\text{PVP}}$: 177.06 ppm, LW

= 215 Hz; PVP/PPDT $\text{C}=\text{O}_{\text{PVP}}$: 176.60 ppm, LW = 291 Hz) (Figure 2b). Therefore, at a level of a few angstroms the two polymers in the synthetic composite do not interact strongly, nor do they change their conformational arrangement, even though the carbonyl of PVP feels a different environment. The small variation in the chemical shifts and the broadening of the resonance of this carbon can be explained considering that a fraction of PVP carbonyls is in close contact with the PPDT chains. For these carbonyls, two competing effects, among others, can be considered: (a) hydrogen bonding with the PPDT amide groups; (b) magnetic susceptibility generated by the aromatic polymer. The formation of hydrogen bond determines a decrease in electron density on the carbonyl and a low field shift of the carbon resonance, this shift usually being on the order of 1 ppm.²⁵ On the other hand, the magnetic susceptibility effect in the solid state can be remarkable; in the case of polyethylene included in an aromatic host (a nanostructured analogue of a composite) a high field shift of 1.67 ppm has been measured.²⁶

$T_{1\rho}(\text{H})$ and $T_1(\text{H})$ are greatly influenced by spin diffusion and can therefore provide useful information about phase dimension. As an example, amorphous polymers are usually characterized only by a single value of proton relaxation time, whereas semicrystalline polymers usually show two $T_{1\rho}(\text{H})$ values, one for the amorphous phase and one for the crystalline, but only one $T_1(\text{H})$.²⁷ The extent of averaging is determined by the time scale of the relaxation time measured. In fact, diffusion of magnetization can be described in the same way as a general diffusion process. The distance traveled by the magnetization may be estimated from the approximated formula:²⁸

$$\langle L \rangle \cong (r_0^2 t / T_2)^{1/2} \quad (2)$$

where t is the relaxation time measured, r_0 the van der Waals radius of the hydrogen atom (1.17×10^{-10} m), and T_2 the transversal proton relaxation time.

Longitudinal relaxation times in the rotating frame of proton nuclei, $T_{1\rho}(\text{H})$, are usually on the order of milliseconds, and the proton magnetization can diffuse over a maximum distance of a few nanometers.²⁹ Instead, the longitudinal proton relaxation time in the laboratory frame, $T_1(\text{H})$, is on the order of a few seconds, and proton magnetization can diffuse over a distance of several tens of nanometers. Cross-polarization experiments appended at the end of the proper pulse sequence can transfer proton magnetization to the carbon nuclei; relaxation times can thus be measured from the point of view of the single blend component. Therefore, using solid-state NMR, it is possible to detect whether a polymer blend is intimate and at what scale (a few angstroms or nanometers). The study of proton relaxation times has been widely carried out to probe the miscibility of a variety of polymer blends; in particular, PVP-based systems have been characterized using $T_{1\rho}(\text{H})$ measurements.^{21,24,30}

$T_{1\rho}(\text{H})$ relaxation decay for neat PPDT and PVP is represented in Figure 3, with the corresponding values given in Table 4. Both polymers present monoexponential decay and, within each polymer, the same $T_{1\rho}(\text{H})$ for all carbon types. This is a clear indication both that spin diffusion averages the local environments and that each polymer presents only one phase (considering phase dimensions of a few nanometers). $T_1(\text{H})$ values

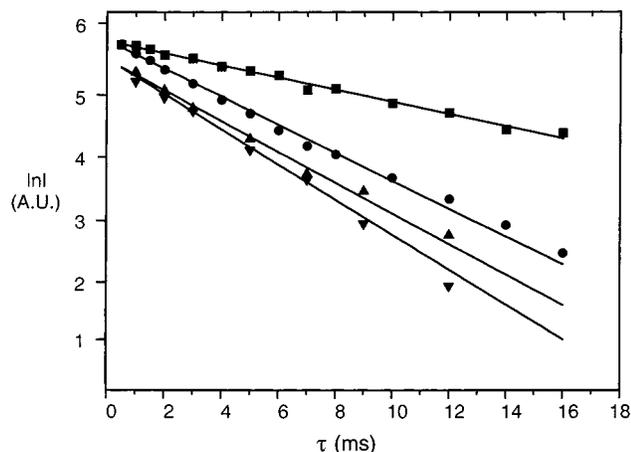


Figure 3. $T_{1\rho}({}^1\text{H})$ proton relaxation times measured from the ${}^{13}\text{C}$ spectra: (■) neat PVP, (●) neat PPDT, (▲) PVP, and (▼) PPDT in sample H-90 obtained by matrix polycondensation using direct synthesis.

Table 4. Proton Spin–Lattice Relaxation Times in the Rotating Frame of PPDT, PVP, and Their Blends and Nanocomposites

sample code	composition and origin	PPDT $T_{1\rho}({}^1\text{H})$ (ms)		PVP $T_{1\rho}({}^1\text{H})$ (ms)	
		C=O	aromatic carbons	C=O	aliphatic carbons
	neat samples	9.4	8.8	17.4	19.9
H-30	direct synthesis	8.3	8.1	9.3	10.0
H-90	direct synthesis	5.8	7.6	6.5	8.7
I-1	PPDT/PVP 750 000	8.7 ^a	8.8 ^a	11.2	12.3
M-1	PPDT/PVP cast from H_2SO_4 solution	6.7	6.5	3.9	3.9

^a Multiexponential.

are considerably different: PPDT shows a $T_{1\rho}({}^1\text{H})$ of 9 ms, whereas PVP has a value of 18 ms. The PPDT/PVP samples obtained using direct matrix polycondensation have a different behavior compared to the pure polymers: indeed, both PPDT and PVP show nearly the same $T_{1\rho}({}^1\text{H})$ values (Figure 3 and Table 4, samples H-30 and H-90). From eq 2 and considering that T_2 , for a polymer at $T < T_g$, is typically 1×10^{-5} s, the scale of mixing based on the measured relaxation times (10 ms) is approximately 3 nm. This means that spin diffusion averages the local differences of proton magnetization on a scale of 3 nm. Therefore, the phases of the pure polymers, if present, are smaller than that value. This result strongly supports the formation of nanocomposites and suggests a model (see later) of matrix polycondensation.

To verify the miscibility of the two polymers, we prepared a blend (M-1) by dissolving PPDT and PVP in H_2SO_4 and then dropwise precipitating the mixture in cooled acetone. The $T_{1\rho}({}^1\text{H})$ relaxation decays are shown in Figure 4, and the values are reported in Table 4. The two polymers present clearly different relaxation behaviors; therefore, this blend obtained by casting is phase separated on the scale of a few nanometers. Degradation products are a likely explanation for the low values of $T_{1\rho}({}^1\text{H})$ measured.

A PPDT/PVP blend obtained by indirect synthesis (sample I-1) was also studied. Figure 5 shows the $T_{1\rho}({}^1\text{H})$ relaxation decays for the composite obtained using PVP with MW = 750 000. They are clearly multiexponential, indicating the presence of some heterogeneity.

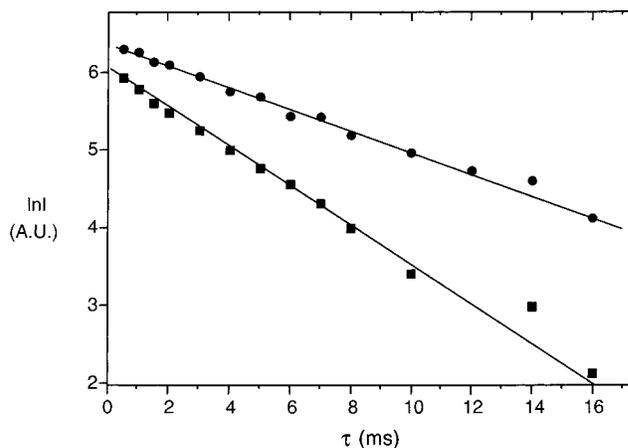


Figure 4. $T_{1\rho}({}^1\text{H})$ proton relaxation times measured from the ${}^{13}\text{C}$ spectra: (■) PVP in the blend M-1 obtained from H_2SO_4 solution, (●) PPDT in the blend M-1 obtained from H_2SO_4 .

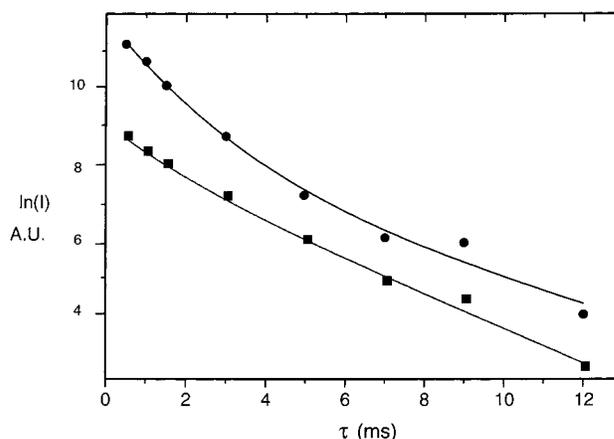


Figure 5. $T_{1\rho}({}^1\text{H})$ proton relaxation times measured from the ${}^{13}\text{C}$ spectra: (■) PVP and (●) PPDT in the sample I-1 obtained by matrix polycondensation using *indirect* synthesis (PVP MW = 750 000).

This result, together with the low viscosity measured for these systems, confirms that the templating polymer has poor control over the polymerization of terephthaloyl chloride, which is more reactive than the corresponding acid. Therefore, presumably, only a fraction of the aramid is polymerized via the template mechanism, the remaining part being polymerized independently without any influence of PVP.

Conclusions

The results herein reported give new emphasis to further research in the field of controlled MW aramid synthesis, with much potential exploitation in various fundamental and technological areas.

In particular, a new model for matrix polycondensation, in which the polymer matrix is a flexible coil characterized by a relatively long macromolecular chain and the daughter polymer is a rigid-rod-like and relatively short chain, must be developed. Indeed, in this case, the growth of the daughter chain just along the flexible matrix (as commonly accepted for template polymerization leading to flexible polymers) does not seem possible. Alternative interpretations are needed. One could be the following: because of the presence of functional groups, able to interact with the host segments, monomer concentration inside the matrix coil is probably much higher than outside. As a result, the

growth of the daughter polymer is favored. At the end of the reaction, the rodlike polymer chains remain entangled inside the matrix, due to both physicochemical and purely physical interactions. In other words, the matrix effect can be more appropriately seen as a topological effect in rigid-rod synthesis, when a coiled host macromolecule is present in the reaction medium.

Solid-state NMR results demonstrate that by matrix-assisted direct polycondensation it is possible to optimize the obtainment of an intimate blend of PPDT and PVP, i.e., of a nanocomposite. The synthetic polymer blend can be seen to be homogeneous in the length scale of a few nanometers, due to the fact that the rigid daughter polymer is forced to mainly grow in close contact with the matrix coil. Thus, for kinetic reasons, this daughter polymer remains entrapped in a nonequilibrium structure. Indirect synthesis and the preparation of the composite by casting does not lead to the same intimate blending. Thus, it would appear that matrix polymerization could be an intriguing procedure for the preparation of homogeneous blends that are otherwise difficult, or practically impossible, to prepare.

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