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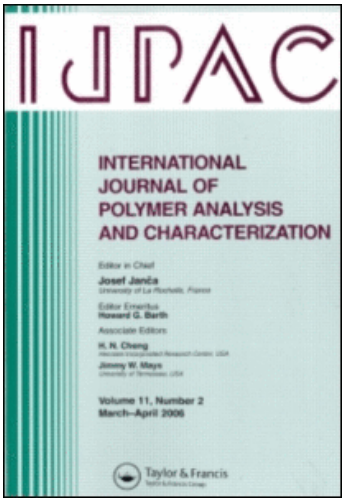

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Associations Between Hydrophibically End-Capped Polyethylene Oxide and Water Soluble (β Cyclodextrin Polymers

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To cite this Article Amiel, C. , Sandier, A. , Sébille, B. , Valat, P. and Wintgens, V.(1995) 'Associations Between Hydrophibically End-Capped Polyethylene Oxide and Water Soluble (β Cyclodextrin Polymers', International Journal of Polymer Analysis and Characterization, 1: 4, 289 — 300
To link to this Article: DOI: 10.1080/10236669508233882
URL: http://dx.doi.org/10.1080/10236669508233882

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Int. J. Polymer Analysis & Characterization
1995, Vol. 1, pp. 289–300
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Associations Between Hydrophibically End-Capped Polyethylene Oxide and Water Soluble β Cyclodextrin Polymers

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(Received July 18, 1994; Revised October 19, 1994)

In this study, polyethylene oxide chains have been hydrophobically end-modified with naphthalene groups (PEO-N), and water soluble ß-cyclodextrin polymers (ß-CD/EP) have been synthesized. An original associating system can be obtained by mixing these two polymers in aqueous solutions. Inclusion complex formation between the hydrophobic moieties of the PEO-N chains and the ß-cyclodextrin cavities of the ß-CD/EP polymers are at the origin of the polymolecular associations. Fluorescence anisotropy measurements allowed the determination of the complexation constants, and the onset of the polymolecular associations have been monitored by viscosimetry. The PEO chain length influence has been studied by using two molecular weights, 6000 and 20000.

KEY WORDS Associating polymers, ß-cyclodextrin, Inclusion complex, Polyethylene oxide, Fluorescence anisotropy, viscosimetry.

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INTRODUCTION

Associating polymers have recently become the subject of extensive research [1–4] with the use of hydrophobically modified polymers. These amphipathic macromolecules are generally obtained from water soluble polymers modified with relatively low amounts of a hydrophobic comonomer (1–5 mol%). They exhibit unusual aqueous solution behavior with the appearance of thickening properties above certain polymer concentrations, due to polymolecular associations. The hydrophobic interactions that occur in order to minimize water-hydrophobe contact are at the origin of the polymolecular associations. In this work, a different class of associating polymer system is proposed. The interchain associations are controlled through more specific interactions which involve complexation of the hydrophobic moieties by the cavities of ß-cyclodextrin containing polymers.

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This paper was originally presented at the Seventh International Society on Polymer Analysis and Characterization Meeting.

The system involves the mixture of two polymers in aqueous solutions: polyethylene oxide chains end capped with naphthalene groups (PEO-N), and water soluble ß-cyclodextrin/epichlorohydrin polymers (ß-CD/EP). The naphthalene end groups have been chosen in order to match the cavity size, a necessary condition for a good inclusion [5]. Associations are schematized in Figure 1. Moreover, the naphthalene groups exhibit fluo-

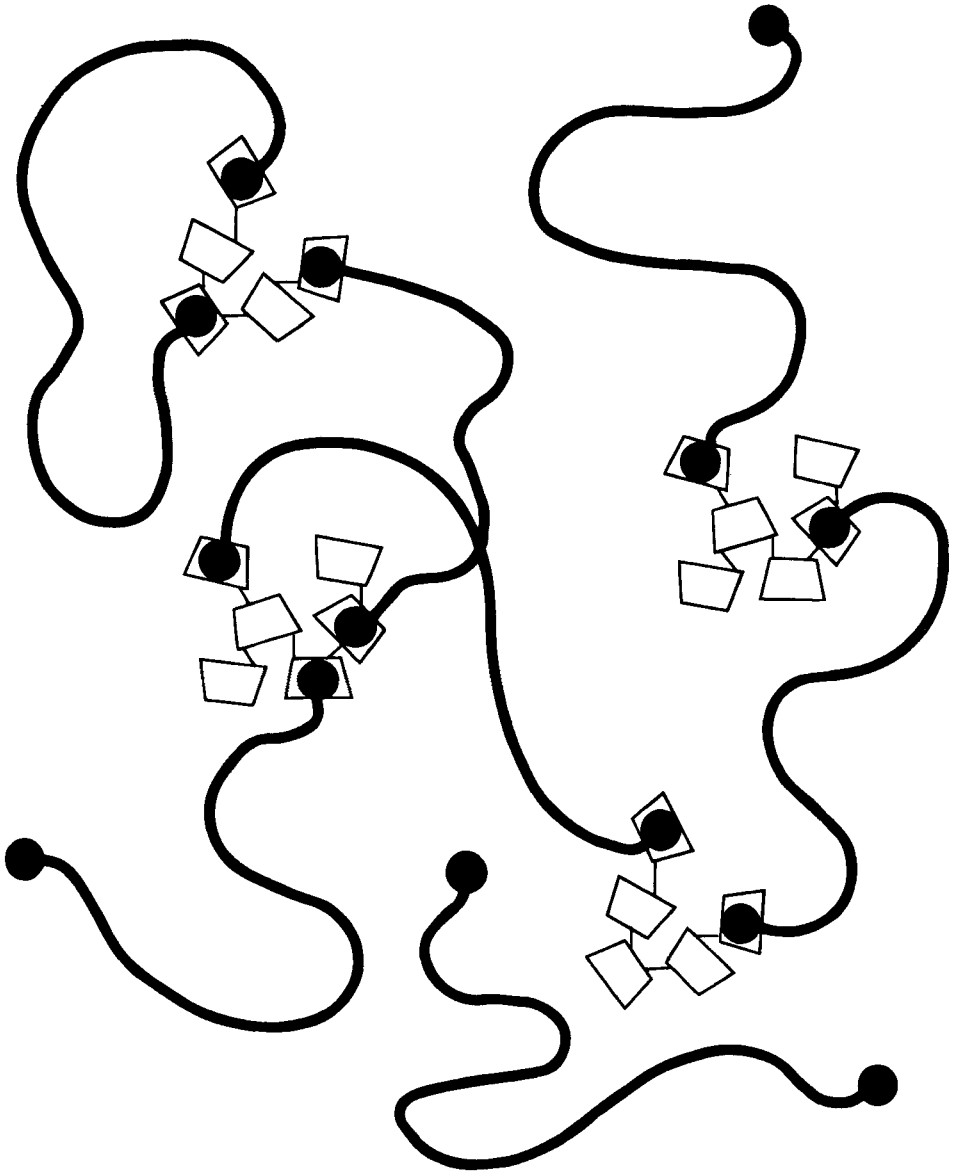

FIGURE 1 Schematic illustration of the interactions between the linear PEO chains end-capped with naphthalene groups and water soluble ß-cyclodextrin polymers. Inclusion complex formations between the naphthalene end groups and the ß-cyclodextrin are at the origin of the associations.

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rescence properties which are affected by the formation of a complex with ß-cyclodextrin. The association properties have been checked through two kinds of measurements: viscosimetry and fluorescence anisotropy. The size influence of the telomeric chains (PEO-N) has been studied using two molecular weights (6000 and 20000) for the PEO precursor.

Fluorescence anisotropy methods can probe with a good sensitivity the extent of the rotational diffusion of the fluorescent label during its fluorescence lifetime [6]. The inclusion of the naphthalene ends inside cyclodextrin cavities, which are linked to a larger structure (the ß-CD/EP polymer), should greatly reduce their rotational diffusion time. A good contrast between the fluorescence anisotropies of the free and complexed probes is therefore expected. This method has been used for the determination of the complexation constant between the naphthalene ends of PEO-N and the cyclodextrin cavities of ß-CD/EP.

Complex formation between the two polymers can either give compact structures (for instance when both ends of PEO-N are included in the same ß-CD/EP polymer) or extended structures, obtained when there are polymolecular associations. Viscosimetry provides information about the macroscopic properties of the medium. The onset of polymolecular associations has been monitored by measuring the viscosity of the system and comparing it to a solution containing the same amount of precursor PEO chains and ß-CD/EP polymers. The parameters for this study are the concentrations of both polymers.

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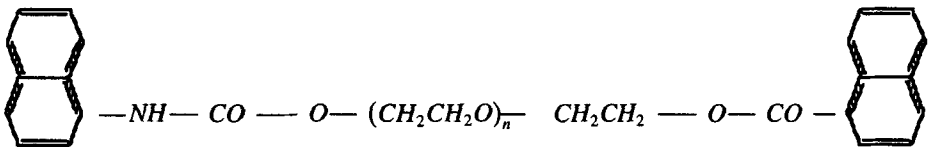
MATERIALS AND METHODS

1-Hydrophobically end-capped polyethylene oxide (PEO-N)

Polymers of polyethylene oxide, molecular weights 6000 and 20000 have been purchased from Merck, Nogent-sur Marne, France. The chain ends have been modified by reaction with 1-naphthyl isocyanate (Aldrich, St. Quentin Fallavier, Fr.) in large excess. PEO was previously dried by heating at 70°C during 8 hours. The reactants were dissolved in dichloroethane and two catalysts were added: dibutyltin dilaurate (Merck) and triethylamine (Aldrich). The reaction bath was heated at 65°C for 5 hours. The modified polymer was purified by addition of activated carbon in aqueous solutions and filtrations. The extent of the end grafting reaction, determined with H nuclear magnetic resonance (NMR) spectroscopy, was 100% for the two molecular weights. The structural formula of PEO-N is the following:



2-Synthesis of the ß-cyclodextrin/epichlorohydrin polymers (ß-CD/EP)

ß-cyclodextrin was a gift from Orsan Company, Paris, France. The ß-cyclodextrin polymer was prepared by crosslinking ß-cyclodextrin, under strongly alkaline conditions, with

epichlorohydrin (Prolabo, Paris, Fr.), the molar ratio being 1/10. The details of the synthesis are described elsewhere [7]. 10 g of ß-cyclodextrin was dissolved in 16 ml of 50% NaOH. 6.9 ml of epichlorohydrin was added and the reaction solution was heated at 30°C for approximately 3 hours. The reaction was stopped by addition of acetone before the gelation point but when the viscosity of the medium was very high. After cooling, the solution was neutralized with HCl and subjected to ultrafiltration (molecular weight cut-off 1000). The reaction yielded 10 g of highly water soluble polymer. The molecular weight distribution, monitored by size exclusion chromatography, showed a characteristic pre-gelation pattern with two populations having approximately the same weight ratio: a population of oligomers, mean molecular weights around 5000 and a population of polymers, molecular weights between 100,000 and 200,000. The ß-cyclodextrin content has been titrated by a colorimetric method using phenolphthalein [7] which loses its color properties (in basic solution) when it is included in ß-cyclodextrin cavities. The ß-CD/EP polymer contained 67 weight % of ß-cyclodextrin.

3- Viscosimetry

The viscosity measurements were carried out with an Ubbelohde type viscometer. The temperature was fixed at 25.0 ± 0.05°C. Solvent and solutions were filtered prior to any measurements.

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4- Fluorescence anisotropy

The fluorescence lifetimes have been determined using a picosecond YAG laser and an experimental set-up described elsewhere [8]. The excitation wavelength was at 266 nm. The steady state fluorescence study was performed on a SLM AMINCO 8000 spectrofluorimeter equipped with a xenon lamp and with a polarization device. All the measurements were carried on at an excitation wavelength of 285 nm, and anisotropies were determined at an emission wavelength of 360 nm. The fluorescence anisotropy r is defined by the following relationship:

$$r = (I\parallel - I\perp)/(I\parallel + 2I\perp) \quad (1)$$

where $I\parallel$ and $I\perp$ are the fluorescence intensities of the vertically and horizontally polarized emission when the sample is excited with vertically polarized light. The anisotropy is related to the rotational correlation time of the probe by the Perrin equation:6

$$r = r_0/(1 + \tau/\phi) \quad (2)$$

where r_0 is the anisotropy which would be measured in the absence of rotational diffusion, τ the fluorescence lifetime and ϕ the rotational diffusion time of the probe. Fluorescence anisotropy is thus a powerful tool for studying the microenvironment of the probes [9]. In our case, the inclusion of the naphthalene ends inside the ß-cyclodextrin cavities of the ß-CD/EP polymers should greatly reduce their rotational diffusion time and, consequently, induce a marked change in the anisotropy values. We can assume that two populations of probes are present in the medium [6,10]:

- free probes, r_f being their anisotropy and n_f their number fraction,
- complexed probes, r_c being their anisotropy and n_c their number fraction ($n_c = 1 - n_f$).

The measured anisotropy is a balanced expression of the two forms:

$$r = [n_f/(n_f + n_c R)]r_f + [n_c R/(n_f + n_c R)]r_c \quad (3)$$

where R is the ratio of the quantum yields of the complexed form over the free one. It has been determined from fluorescence lifetime measurements: $R = 1.86$.

RESULTS AND DISCUSSION

1- Complexation Constant Measurements

The complexation between the naphthalene ends and ß-cyclodextrin is represented by the following equilibrium, assuming a simple 1:1 host/guest complex:

$$N + CD \leftrightarrow NCD \quad (4)$$

where N represent the naphthalene groups, CD the cyclodextrin units of the polymers and NCD the complex. The complexation constant K_c in L/mol is:

$$K_c = [NCD]/[N]\,[CD] \quad (5)$$

The values in brackets represent the molar concentrations of the species previously defined. If the cyclodextrin units are in large excess in the solution, the free cyclodextrin concentration [CD] can be approximated by the total concentration in cavities $[CD]_0$. The percentage of probes which are in the free state:

$$n_f = [N]/[N]_0 \quad (6)$$

$[N]_0$ being the total concentration in probes, can be estimated from Equation (5) and the mass conservations of N and CD.

$$n_f = 1/(1 + K_c[CD]_0) \quad (7)$$

The CD concentration dependence of n_f can be included in the expression for the anisotropy (3). The following relationship is deduced:

$$(r - r_f)^{-1} = (r_c - r_f)^{-1}(RK_c)^{-1}[CD]_0^{-1} + (r_c - r_f)^{-1} \quad (8)$$

r_f is measured independently in a solution of PEO-N. Thus a reasonable estimate of K_c can be obtained from a plot of $1/(r - r_f)$ versus $1/[CD]_0$. The intercept gives the inverse of the anisotropy difference between the free and the complexed probe $r_f - r_c$. The ratio of the intercept divided by the slope gives directly the product $R \cdot K_c$.

Solutions with fixed concentrations in naphthalene groups (3.10^{-4} mol/L for PEO-N 6000 and 10^{-4} mol/L for PEO-N 20000) and with increasing cyclodextrin concentrations of ß-CD/EP (larger than 5.10^{-3} M/L) were prepared and their anisotropy have been mea-

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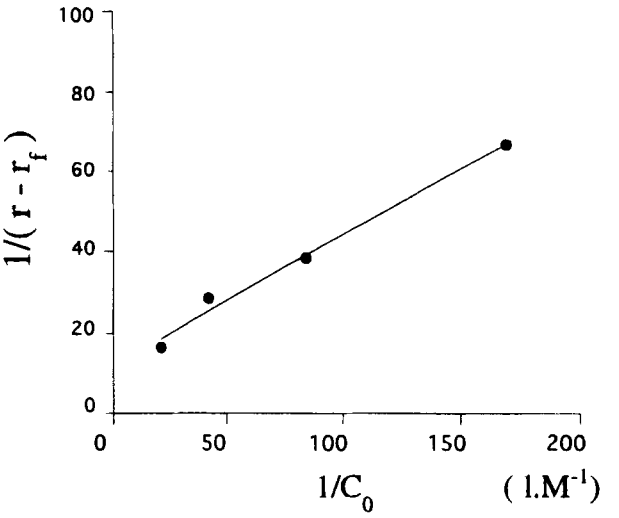

FIGURE 2 Complexation constant determination for the PEO-N 20000/ß-CD/EP system. Double reciprocal plot of $r - r_f$ as a function of the ß-cyclodextrin molar concentrations C_0, where r is the fluorescence anisotropy of the naphthalene groups and r_f its value when there is no complexation.

Table I

Measured fluorescence anisotropy differences ($r_c - r_f$) and complexation constants (K_c).

	$r_c - r_f$	K_c (L/mol)
PEO-N 6000	0.102	26
PEO-N 20000	0.113	12

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sured. Variations of $(r - r_f)^{-1}$ as a function of $[CD]_0^{-1}$ for PEO-N 20000 are represented on Figure 2. In all the cases, a linear plot was obtained, justifying the assumption of a 1:1 complexation. Complexation constants, as well as the anisotropy differences, have been determined and reported in Table I for the two modified PEOs.

The anisotropy difference between the free and complexed form of the probe is high (0.1) showing that the inclusion of the naphthalene groups inside the cavities markedly reduces their mobilities. The complexation constants are relatively low compared to that of naphthalene with ß-cyclodextrin [11] (around 600 L/mol). Moreover these values are a decreasing function of the PEO chain length. This can be understood as an excluded volume effect reducing the entropy of the chain when one end is immobilized [12].

2-Viscosity Measurements

a- Hydrophobically modified PEO The hydrophobic ends of the PEO-N polymers can give them associating properties, as has been seen for different hydrophobically modified PEOs [2, 13–15]. PEO-N specific viscosities have been measured as a function of the polymer concentration and their variations have been compared to the ones

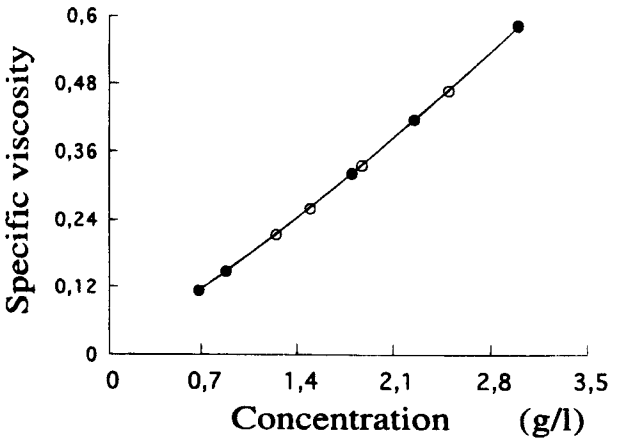

FIGURE 3 Comparison of the specific viscosities of PEO (○) and PEO-N (●) of molecular weights 6000 as a function of the PEO concentrations.

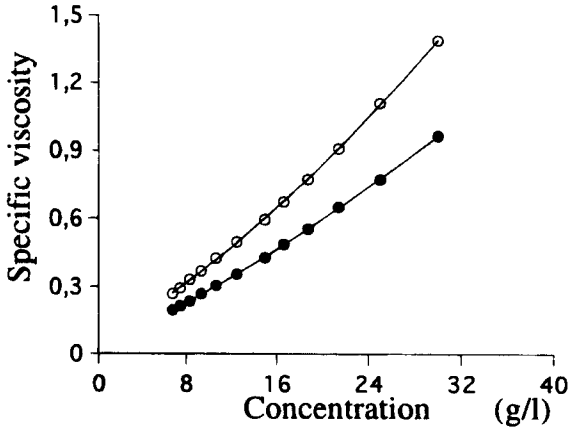

FIGURE 4 Comparison of the specific viscosities of PEO (○) and PEO-N (●) of molecular weights 20000 as a function of the PEO concentrations.

of the precursor chains, as is presented on Figures 3 and 4 for PEO 6000 and PEO 20000, respectively. In the concentration range checked (up to 30 g/L), no thickening effects have been detected. For the smaller polymer, the plots superimpose on each other, showing that there are no detectable associations between the naphthalene groups. Surprisingly, the specific viscosity of PEO-N is always smaller than the specific viscosity of PEO for the largest polymer. Thus, the PEO-N chains of molecular weight 20000 seem to have a more compact structure than the precursor chains. This can be due to intra-molecular associations between the naphthalene ends or, more likely, to hydrogen bond formation between the urethane functions that link the hydrophobic ends to the polymer and the PEO units. The different behavior of PEO-N 6000 and 20000 may be attributed to flexibility differences [16].

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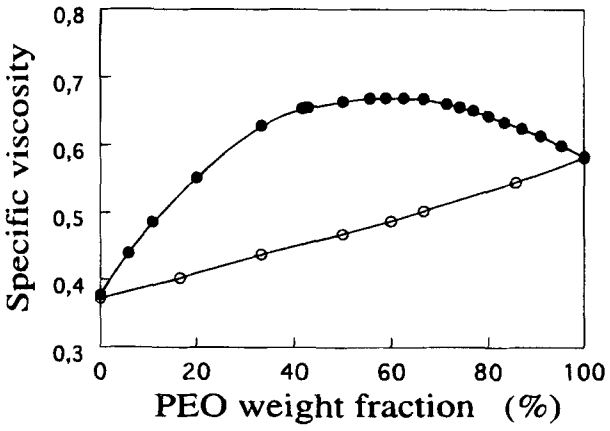

FIGURE 5 Specific viscosities of PEO-N 6000 and ß-CD/EP mixtures as a function of the PEO weight fractions (●) when the total polymer concentration is kept constant at 30 g/L. The viscosity variations of the mixtures containing the precursor PEO 6000 are also reported (○).

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b- Mixing PEO-N and ß-CD/EP polymers Thickening effects are observed when the two polymers are put together, as is shown on Figure 5 for a PEO molecular weight of 6000. The total polymer concentration (PEO-N and ß-CD/EP) was held constant, 30 g/L in this exemple, and the specific viscosities have been reported as a function of the weight fraction of PEO. The higher viscosities measured for the mixture with modified PEO than for the mixture with the precursor cannot be attributed to hydrophobic associations of the naphthalene ends (see previous section). Inclusion of the naphthalene ends into the cavities of the ß-CD/EP polymers, giving rise to polymolecular associations, is at the origin of this phenomenon. The plot in Figure 5 shows a maximum which can be seen as optimum conditions for the formation of aggregates, in the conditions of the experiment (constant total polymer concentration).

ß-CD/EP polymers and PEO are incompatible polymers which form two-phase systems at high concentrations [16]. The two components can be compatibilized when an attractive interaction between them is introduced, as is the case when the ends of the PEO-N polymers are complexed with the ß-cyclodextrin of the ß-CD/EP polymers. This effect has been observed for PEO-N of molecular weight 20000, as is presented in Figure 6. Specific viscosities have been measured for mixtures where the total polymer concentration was held constant at 160 g/L. Only one homogeneous phase was obtained and high viscosities, reaching a maximum at a certain composition, have been observed. No measurements have been reported for the mixtures with the precursor PEO because two phase systems were obtained in these conditions.

c- Parameters affecting the rheological behavior of the polymer mixture ß-CD/EP polymers can be envisioned as compact and quite rigid objects, as expected with ramified structures. This is confirmed by its low intrinsic viscosity ($8.7\ 10^{-2}$ dL/g) and by the large mobility reduction (measured by fluorescence anisotropy) of the naphthalene ends when

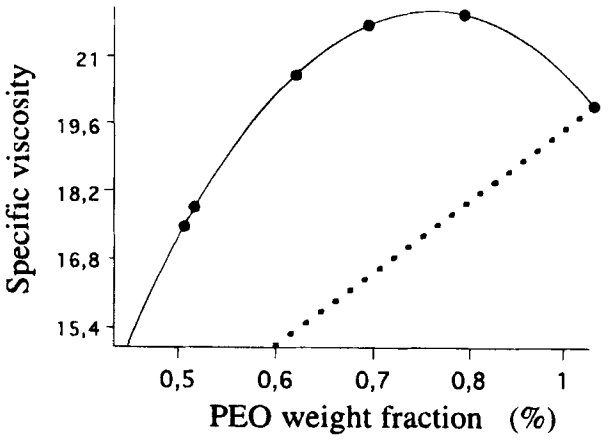

FIGURE 6 Specific viscosities of PEO-N 20000 and ß-CD/EP mixtures as a function of the PEO weight fractions (●) when the total polymer concentration is kept constant at 160 g/L. No measurements have been reported for the mixtures with the precursor PEO 20000 in the dashed line region because two-phase systems are obtained in this concentration range.

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they are complexed inside the polymer cavities. In order to understand the mechanisms leading to polymolecular associations, the size of the ß-CD/EP polymers is neglected in a first and rough approximation. The connectivity properties of the medium are then only controlled by the PEO-N flexible chains. Two parameters are determining the macroscopic properties of the medium:

- the percentage of links established by the PEO-N chains. This is the fraction of complexed naphthalene groups. Knowing the concentrations in both components in the mixture, this can be determined using EQUATION (5) and K_c values of Table I.
- the distance between the PEO-N coils in the solution. The probability of formation of small compact structures is large when the PEO-N chains are far from each other and conversely polymolecular associations are favored when the coils are close to contact. The PEO-N concentrations have thus to be compared to the concentration C* at which the coils start to overlap. C* is approximately two times larger for PEO-N 6000 (~ 30g/L) than for PEO-N 20000 (15 g/L).

Specific viscosities of mixtures of PEO-N and ß-CD/EP having the same weight ratio are plotted as a function of the PEO concentration in Figures 7 and 8 for PEO molecular weights of 6000 and 20000, respectively. The fractions of complexed naphthalene ends, estimated from the K_c values of Table I, are varied from 0 to 33% for PEO 6000 and from 0 to 17% for PEO 20000 as the PEO concentration is increased till 30 g/L. Despite lower fractions of links, larger viscosity enhancements are observed for the larger polymer than for the smaller one. Moreover, the onset of the thickening effects is occurring at a lower concentration (around 7 g/l) for PEO 20000 than for PEO 6000 (around 14 g/L). These concentrations are about two times lower than the C* values. This trend indicates that it is not justified to neglect the size of the ß-CD/EP

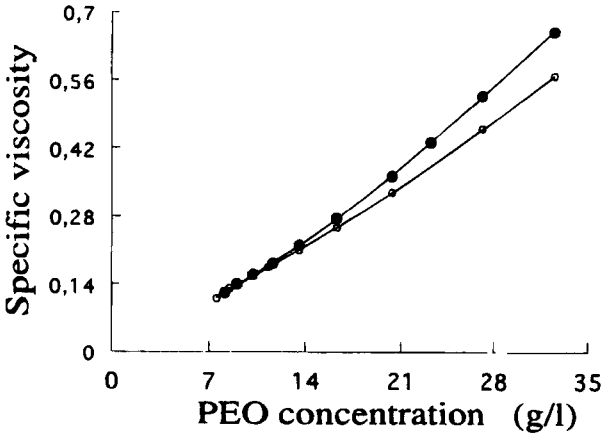

FIGURE 7 Variations of the specific viscosities of mixtures PEO-N 6000 and ß-CD/EP having the same weight ratio as a function of the PEO concentrations (●). Comparison with the specific viscosities of the mixtures with the precursor PEO 6000 (○).

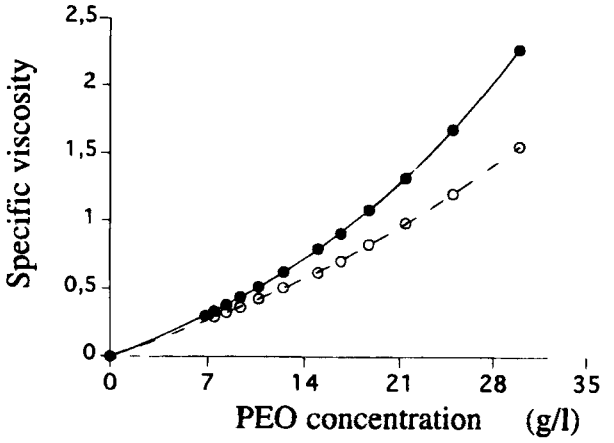

FIGURE 8 Variations of the specific viscosities of mixtures PEO-N 20000 and ß-CD/EP having the same weight ratio as a function of the PEO concentrations (●). Comparison with the specific viscosities of the mixtures with the precursor PEO 20000 (○).

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polymers as was assumed at the beginning of the discussion. In fact, both polymers may contribute to the connectivity properties and the second parameter could be replaced by the distance between chains (both PEO-N and ß-CD/EP) in the solution. Nevertheless, the increase of the PEO chain length has two opposing effects: to decrease the fraction of links by decreasing the complexation constant K_c and to increase the probability of polymolecular associations by decreasing the C* value. The second effect seems to be dominant in this study.

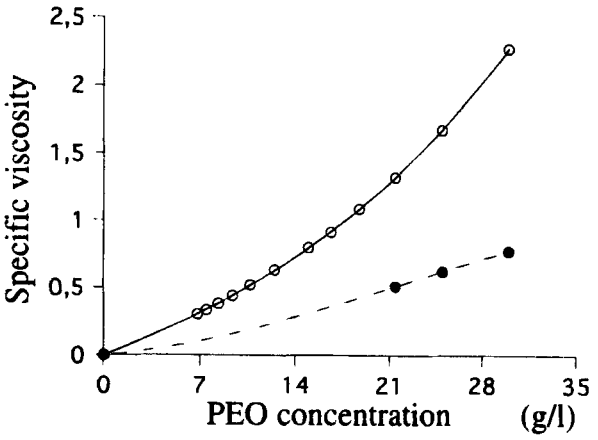

FIGURE 9 Addition of a competitor p-nitrophenol. Comparison of the specific viscosities of PEO-N 20000 and ß-CD/EP having the same weight ratio for samples with (●) and without (○) p-nitrophenol.

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d- Reversibility of the associations by addition of a competitor The associations in the polymer mixtures can be destroyed by addition of a competitor that would displace the naphthalene ends from the cavities. P-nitrophenol has a complexation constant with ß-cyclodextrin of 380 L/mol [18], much larger than the one of the naphthalene ends. In solutions containing PEO-N 20000 and ß-CD/EP in 1/1 weight ratio, p-nitrophenol has been added in the same molar ratio as the cyclodextrin units. The specific viscosities have been measured for the solutions with and without p-nitrophenol at different concentrations. The measurements are reported on Figure 9. Upon addition of the competitor, the viscosities are markedly reduced, showing that the polymolecular associations are destroyed by the preferential complexation of p-nitrophenol. Surprisingly, the specific viscosities of the solutions containing the competitor are even lower than expected. This can be attributed to polar interactions of p-nitrophenol with PEO chains.

CONCLUSION

An original associating polymer system has been described in this study. Inclusion complex formations are at the origin of the associations between an hydrophobically modified PEO and a water soluble ß-cyclodextrin polymer. Associations between the two polymers have been demonstrated through both microscopic and macroscopic analysis of the properties of the medium: fluorescence anisotropy for the determination of the complexation constants and viscosimetry for the onset of the polymolecular associations. The PEO chain length has two opposing effects on the associations: the complexation constant is a decreasing function of the chain length, and the probability of polymolecular associations, on the contrary, is an increasing function of the chain

length. It has been shown that the larger PEO-N chains have better thickening properties, and association occurs at lower concentration for the larger chains than for the smaller ones.

Due to the relatively low complexation constants, the thickening properties are very moderate compared to the very high viscosity enhancements that can be observed with associating polymers [1–4,12–14]. A natural extension of this work will be to modify the PEO ends with hydrophobic groups chosen for their high complexation constants with ß-cyclodextrin.

Acknowledgments

We would like to thank A. Deratani, M. Guillaume, L. Lelievre and E. Renard for their help in the synthesis and characterization of the ß-CD/EP polymers.

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