NEW ASSOCIATING POLYMER SYSTEMS INVOLVING WATER SOLUBLE β-CYCLODEXTRIN POLYMERS.

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ABSTRACT

Original associating systems have been obtained by mixing hydrophobically end-capped polyethylene oxide and water soluble β-cyclodextrin polymers in aqueous solutions. The hydrophobic ends of the PEO polymers, naphtyl and adamantyl groups, have been chosen in order to match the β-cyclodextrin cavities. Inclusion complex formation between the PEO terminal groups and β-cyclodextrin are at the origin of polymolecular associations. Complexation constants have been determined by fluorescence methods, using a fluorescent probe 1-8 ANS as a competitor for complexation against the adamantyl groups or directly checking the fluorescence of the naphtytl groups by fluorescence anisotropy measurements. The onsets of the polymolecular associations have been monitored by viscosimetry.

1. INTRODUCTION

Associating polymers have recently become the subject of extensive research with the use of hydrophobically modified polymers [1]. These amphipathic macromolecules are generally obtained from water soluble polymers modified with relatively low amounts of 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 contacts are at the origin of the polymolecular associations. In this work, a new class of associating polymer systems is proposed. The principle is to add a water soluble β-cyclodextrin polymer to an aqueous solution of amphiphilic polymer.

The β–cyclodextrin polymers are promoting the associations between the amphiphilic polymers by forming inclusion complexes between the hydrophobic moieties and the β-cyclodextrin cavities. In this study, the water-soluble β-cyclodextrin polymers are formed by polycondensation with epichlorhydrin under strongly alkaline conditions. The amphiphilic polymers are hydrophobically end-capped polyethylene oxide where the hydrophobic ends have been chosen in order to match the β-cyclodextrin cavities. Two kinds of terminal groups have been used: naphtyl groups substituted in position 1 or 2, whose interactions can be easily studied by fluorescence methods, and adamantyl groups which possess higher affinities for the β-cyclodextrin cavities.

The complexation constants have been determined by fluorescence methods: fluorescence anisotropy measurements have been developped for naphtalene end-capped PEO while a fluorescent probe, 1-8 ANS, has been used for adamantane end-capped PEO. In the last case, the measurements involved a competitive complexation between the ANS probes and the adamantyl groups.

The onsets of the polymolecular associations have been monitored by viscosimetry, by comparing the viscosity of the system at a certain concentration to the one of a solution containing the same amount of precursor PEO chain and β–CD polymer. The influences of the nature of the end- capping group as well as the PEO chain length have been

studied.

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Hydrophobically end-capped PEO

Polymers of polyethylene oxide, molecular weight 6000, 20000 and 35000 have been purchased from Merck, France. PEO-N1 and PEO-AD were obtained by reaction of the OH terminal functions with isocyanate groups, 1-naphtyl isocyanate and 1-adamantyl isocyanate respectively (Aldrich, France). PEO-N2 was obtained by reaction of the OH groups with the acid chloride group of 2-chlorocarbonylnaphtyl (Aldrich, France). N-Naphtyl ethyl carbamate (model-N1) was obtained by reaction of 1-naphtyl isocyanate with ethanol. The structural formula of the modified polymers are schematically represented on figure 1.
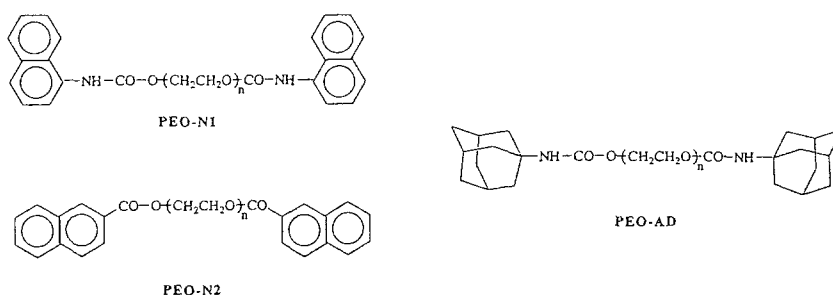

Fig.1 Structural formula of the end-capped PEO.

The extent of the end grafting reactions were determined with ^{1}H NMR spectroscopy and the results are reported in table 1.

TABLE 1. Characterization of the end-capped PEO

Polymer	Molecular weight	% grafting
PEO-N1	6000	98
PEO-N1	20000	96
PEO-N2	6000	76
PEO-AD	6000	97
PEO-AD	20000	84
PEO-AD	35000	75

2.1.2. β-cyclodextrin polymers (β-CD/EP)

β-cyclodextrin was a gift from Orsan company, France. The β-cyclodextrin polymers (β-CD/EP) were prepared by crosslinking β-cyclodextrin under strongly alkaline conditions with epichlorhydrin (Prolabo, France), the molar ratio being 1/10. The reaction was conducted until the immediate vicinity of the gelation point was reached, in order to obtain relatively high molecular weight of water soluble β-CD polymers. The synthesis and the characterization of these polymers have been described in details elsewhere [2].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 weight around 5000 and a population of polymers , molecular weights higher than 200,000. The β-cyclodextrin content , titrated by ^{1}H NMR spectroscopy, was 65 weight %.

2.2. Methods

2.2.1. Fluorescence anisotropy

The fluorescence studies were performed on a SLM AMINCO 8000 spectrofluorimeter eqipped with a xenon lamp and with a polarization device. The fluorescence anisotropy measurements were carried on at an excitation wavelength of 285 nm and emission wavelength of 360 nm. The inclusion of the naphtyl probes inside the cavities of the β-CD/EP polymers does not induce a marked change in the spectral character of the probes: the ratio of the quantum yields of the complexed form over the free one is R=1.86, determined from fluorescence lifetime measurements [3]. However, the complexation of the probes greatly reduces their rotationnal diffusion time and consequently largely increases their fluorescence anisotropy [4]. From measuring the anisotropy of the free probe in the absence of β-CD/EP , the complexed probe with an excess of β-CD/EP and the anisotropy at an intermediate β-CD level, one can easily determine the complexation constant K_c [5]. The concentration of PEO-N was held constant at a value of 2 g/l and the concentration of β-CD/EP was varied in the range 10 - 80 g/l.

2.2.2. Competitive complexation using a fluorescent probe 1,8 ANS

Since the adamantyl groups are not fluorescent, a fluorescent probe 1-anilino 8-naphtalene sulfonic acid 1-8 ANS (purchased from Sigma, France) has been used as a competitive inhibitor [6][7]. The association constant of 1-8 ANS with β-CD/EP polymers were determined from dependencies of fluorescence intensity of ANS on the concentration of β-CD. For this, the concentration of ANS was fixed at 10^{-5} M . In order to have a medium of constant polarity, unmodified PEO has been added at a fixed concentration of 17.5 g/l .The concentration range of β-CD was 0.2 - 8 mM. The association constants of the PEO adamantyl groups with β-CD were determined by following the fluorescence intensity of the ANS - β-CD/EP solutions at fixed adamantyl concentration (1mM) as a function of the β-CD concentration . In these solutions, the total concentration in PEO was held constant at 17.5 g/l by adding the appropriate quantity of unmodified PEO.

2.2.3 Viscosimetry

The viscosity mesurements 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 mesurements.

3. RESULTS AND DISCUSSION

3.1 Complexation constant measurements

The complexation constants have been measured by the two fluorescence methods and the values are reported on table 2.

TABLE 2: Complexation constants between PEO end capped polymers and β-CD/EP

	PEO molecular weight	K_c (M^{-1})
Model-N1	44	740
PEO-N1	6000	26
PEO-N1	20000	12
PEO-N2	6000	400
PEO-ADAM	6000	3200
PEO-ADAM	20000	2300
PEO-ADAM	35000	2000

The results obtained for PEO-N1 and PEO-N2 of the same PEO molecular weight (6000) show the same trend as reported in the literature for naphtyl groups substituted in position 1 or position 2 [8]: the complexation constant is much higher for PEO-N2 than for PEO-N1.The inclusion of the naphtyl groups being axial , this effect has been attributed to a deeper penetration of the 2-naphtyl group into the cyclodextrin cavities as it does not experience any hindrance from the substituant unlike the 1-naphtyl group.

The model-N1 molecule has been synthesized and its complexation constant measured in order to study the influence of the PEO chain on the complexation behavior. The results show that the complexation constants are sharply decreasing as a function of the PEO chain length: K_C has decreased by a factor of the order of 60 between model-N1 and PEO-N1 20000. This behavior can be attributed to an excluded volume effect reducing the entropy of the chain when one or both ends are linked to cyclodextrins. The PEO chain length influence has also been studied for the PEO-AD polymers with 3 PEO molecular weights: 6000, 20000 and 35000. Again, the K_C values are decreasing as a function of the PEO chain length but the rate is lower. At this point, we should recall that the K_C measurements are done at different experimental conditions for the polymer bearing naphtyl or adamantyl end groups: the PEO concentration (2g/l) was lower than the chain overlapping concentrations for the first ones, while for the other ones the PEO concentration was fixed at a higher value (17.5 g/l) which is in the semi-dilute range for PEO 20000 and 35000' .

3.2. Viscosity measurements

The hydrophobic ends of the modified PEO polymers can give them associating properties, as it is usually observed with the HEUR polymers which are PEO end-capped with alkyl chains of different lengths (C10 to C20) [9]. Specific viscosities of the modified PEO have been measured as a function of the concentration in the range 5 to 40 g/l and compared to the ones of the precursor PEO chains. No thickening effects have been observed . Moreover the viscosities of the modified polymers are equal to the ones of the unmodified polymers within the range of uncertainty of the measurements. The viscosity measurements being done at relatively high shear rates imposed by the capillary viscometer, these results do not necessarily imply that there is no autoassociations of the end groups. Nevertheless, these eventual autoassociations give negligible viscosity effects compared to the associations with the β-CD/EP polymers, as will be seen below.
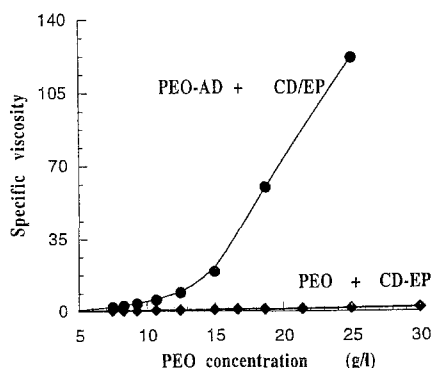

Fig.2 Specific viscosities of mixtures PEO-AD 20000 and β-CD/EP having a weight ratio 1.5. Comparison with the specific viscosities of mixtures containing the precursor PEO 20000.

Thickening effect are obtained when the two polymers are put together, as is shown on figure 2 for PEO-AD 20000 mixed with β-CD/EP in a weight ratio 3/2. Specific viscosities are plotted as a function of the PEO concentration and compared to the specific viscosities of the equivalent mixtures containing unmodified PEO 20000. As it has been observed for associating polymers, the viscosity increases sharply above a certain critical concentration (around 10 g/l for PEO-AD 20000) which corresponds to the onset of

extended polymolecular associations. The probability to form extended structures by associations of the two polymers is controlled both by the percentage of links established by inclusion complex formation and by the connectivity of the system. The percentage of links can be easily calculated from the complexation constant K_C and the concentrations of the two polymers. For instance, one expects that a majority of the terminal PEO groups form links when both concentrations of terminal groups and β–CD are higher than $1/K_C$, that is for PEO concentrations higher than 4.5 g/l in the case of PEO-AD 20000. On the other hand, the probability to link the two terminal groups of a PEO chain to two different β-CD/EP polymers is increased when the chains are close to contact, that is for concentrations higher that critical overlapping concentrations of the heteropolymer system.

The influence of the Kc values has been studied on PEO 6000 grafted with three different groups: 1-naphtyl, 2-naphtyl and adamantyl giving complexation constants 26, 400 and $3200 \, M^{-1}$ respectively. The specific viscosities of the mixtures of modified PEO and β-CD/EP, weight ratio 3/2, have been reported on figure 3 as a function of the PEO concentration. Very low thickening effects are observed for PEO-N1 which forms only 30% links at 30g/l while higher viscosities have been obtained for PEO-AD which possess a high enough K_C value to form more than 80% links in the concentration range explored. From these results, it is clear that better associating properties are obtained with PEO bearing adamantyl end groups.
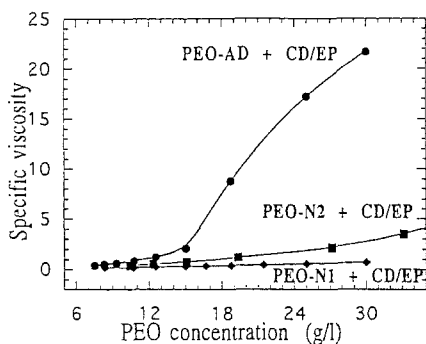

Fig. 3 Specific viscosities of mixtures β-CD/EP and PEO 6000 modified with three different end groups 1-naphtyl (N1), 2-naphtyl (N2) and adamantyl (AD).

The influence of the PEO chain length has been studied using three different molecular weights 6000, 20000 and 35000 of PEO-AD. The specific viscosities of their mixtures with β-CD/EP (weight ratio 3/2) have been measured as a function of the PEO concentration, as well as the specific viscosities of the equivalent mixtures with unmodified PEO. Relative viscosities which are the viscosity ratios of the mixtures with PEO-AD over mixtures with PEO are reported on figure 4. The higher viscosity enhancement is obtained for PEO 20000 and the enhancement is much lower for PEO 35000 than for PEO 6000. Obviously, there is an optimum of the thickening properties for PEO molecular weights around 20000, resulting from the occurence of different opposing effects. The connectivity of the system is increased as the PEO chain length is increased giving higher probability of network formation, but conversely the concentration in end groups is decreased giving lower elastic modulous to the structures formed. On the other hand, the percentage of links calculated from the complexation constants (table 2) are qualitatively comparable (around 80%) for the 3 PEO molecular weights in the concentration range 10 - 30 g/l, but the lower grafting ratio (75%) of adamantyl groups on PEO 35000 (table 1) could partially explain the unexpected behavior of PEO-AD 35000.

One can notice on figure 4 that the relative viscosities seem to reach plateau values at high PEO concentrations for PEO 6000 and 20000. Viscosity measurements have been reproduced in this concentration range using an other experimental set-up allowing low shear rates $(0.01 - 10 \ s^{-1})$ and the same viscosities have been obtained. Thus non-newtonian behavior of the polymolecular agregates do not seem to be at the origin of this phenomenom. The saturation of the viscosities could rather be interpreted as a levelling at high concentration of the sizes of the agregates. Unmodified PEO and β-CD/EP are known to be incompatible polymers which form two-phase systems at high concentration [10] . Thus the formation of structures of growing size might not be favored by the vicinity of the binary transition and rather limiting sizes might be obtained similarly to what is observed in micellar solutions.
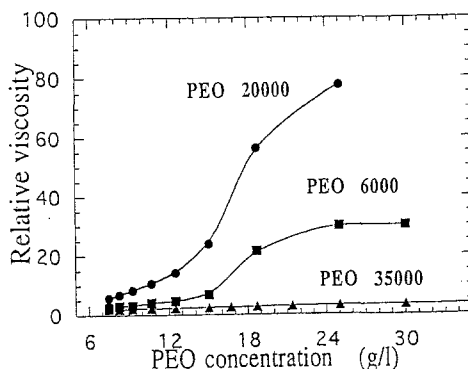

Fig.4 Influence of the PEO molecular weights.Relative viscosities are viscosity ratio of mixtures (3/2 w/w) β-CD/EP and PEO-AD over the equivalent mixtures with unmodified PEO.

4 . CONCLUSION

An original associating polymer system has been described in this study. Inclusion complex formation are at the origin of the associations between hydrophobically end-capped PEO and water soluble β-cyclodextrin polymer. Associations have been demonstrated through both microscopic and macroscopic analysis of the properties of the medium: fluorescence spectroscopies for the determination of the complexation constants and viscosimetry for the onset of the polymolecular associations. The results have shown that the complexation constants are not only dependant on the nature of the end groups (higher values are obtained with adamantyl than with naphtyl groups) but also on the length of the PEO chain: the complexation constants are a decreasing function of the chain length. Thickening properties have been observed by viscosimetry above certain polymer concentrations. The polymolecular associations, which are at the origin of this unusual behavior are both controlled by the connectivity of the system (increasing function of the PEO chain length) and the percentage of complexed groups (decreasing function of the PEO chain length). An optimum of the thickening properties have been observed for a PEO chain length of ca 20000. No network formation has been observed and the limiting growth of the polymolecular agregates has been attributed to the repulsive interactions of PEO and β-CD/EP polymers.

ACKNOWLEDGEMENTS

REFERENCES

[1] Glass, J. E. , Polymers in Aqueous Media: performance through associations, Advances in Chemistry Series 223, (American Chemical Society, Washington DC, 1989).

[2] Renard, E., Deratani, A.,   Sebille, B., Preparation and characterization of water soluble high molecular weight β-cyclodextrin - epichloridrin polymers, *European Polymer Journal*, in press.

[3] Amiel, C., Sandier, A., Sebille, B., Valat, P., Wintgens, V., Associations between hydrophobically end-capped polyethylene oxide and water soluble β-cyclodextrin polymers, *Int. J. Polymer Analysis & Characterization*, **1**, 289-300 (1995).

[4] Lakowitcz, J. R., Principles of fluorescence spectroscopy, Plenum Press, New York (1983).

[5] Nakashima, K., Anzai, T., Fujimoto, Y., *Langmuir*, **10**, 658 (1994).

[6] Park, J. W., Song, H. J., *J. Phys. Chem.*, **93**, 6454-6458 (1989).

[7] Catena, G. C., Bright, F. V., *Analytical Chemistry*, **61**, 905-909 (1989).

[8] Pitchumani, K., Vellayappan, M., Complex formation of nitrobenzoic acids and some naphtalene derivatives with β-cyclodextrin, *Journal of Inclusion Phenomena and Molecular Recognition in Chemistry*, **14**, 157-162 (1992).

[9] Annable, T., Buscall, R., Ettelaie, R., Whittlestone, D., The rheology of solutions of associating polymers: comparison of experimental behavior with transient network theory, *J. Rheol.*, **37**, 695-726 (1993).

[10] Ekberg, B., Sellergren, B., Olsson, L., Mosbach, K., *Carbohydrate Polymers*, **10**, 183 (1989).