NEW ASSOCIATING HETEROPOLYMERS INVOLVING WATER SOLUBLE ß-CYCLODEXTRIN POLYMERS

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INTRODUCTION

Associating polymers [1] 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 heteropolymers is proposed. The principle is to add a water soluble ß-cyclodextrin polymer to an aqueous solution of amphiphilic polymer.

The ß-cyclodextrin polymers are promoting the associations between the amphiphilic polymers by forming inclusion complexes between the hydrophobic moieties and the ß-cyclodextrin cavities. In this study, the water-soluble-ß-cyclodextrin polymer (ß-CD/EP) are formed by polycondensation with epichlorohydrin under strongly alkaline conditions [2]. The amphiphilic polymers are hydrophobically end-capped polyethylene oxide where the hydrophobic ends have been chosen in order to match the ß-cyclodextrin cavities [3] and [4]. 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 ß-cyclodextrin cavities.
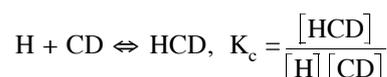
The complexation constants have been determined by fluorescence methods: fluorescence anisotropy measurements [3] have been developed for naphtalene end-capped PEO while a fluorescent probe, 1-8 ANS, has been used for adamantane end-capped PEO [4]. In the last case, the measurements involved a competitive 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 ß-CD polymer. The influences of the nature of the end-capping group as well as the PEO chain length have been studied.

1 COMPLEXATION CONSTANT MEASUREMENTS

The hydrophobic moieties of the telechelic PEO might undergo inclusion complex formation with the cyclodextrin cavities beared by ß-CD/EP polymer:

$$H + CD \Leftrightarrow HCD, \ K_c = \frac{[HCD]}{[H][CD]}$$

[H], [CD] and [HCD] are respectively the molar concentrations in free hydrophobic groups, free CD and bound CD. K_c is the complexation constant in $1M^{-1}$. The complexation constants have been measured by the two fluorescence methods which have been described elsewhere [3] and [4] and the values are reported on Table 1.

TABLE 1

Complexation constants between PEO end capped polymers and ß-CD/EP

	PEO molecular weight	K_c $(1M^{-1})$
Model-N1	44	740
PEO-N1	6 000	26
PEO-N1	20 000	12
PEO-N2	6 000	400
PEO-ADAM	6 000	3 200
PEO-ADAM	20 000	2 300
PEO-ADAM	35 000	2 000

PEO-N1, PEO-N2 and PEO-ADAM are PEO whose extremities have been modified with respectively 1-naphtyl, 2-naphtyl and 1-adamantyl groups. 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 [5]: 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 cavity as it does not experience any hindrance from the substituant unlike the 1-naphtyl group.

The model-N1 molecule (N-naphtyl ethyl carbamate) has been synthetized 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 20 000. 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-ADAM polymers with 3 PEO molecular weights: 6000, 20 000 and 35 000. 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 underline that the K_c measurements are done at different experimental conditions for the polymers bearing naphtyl or adamantyl end groups: the PEO concentration (2 g/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 20 000 and 35 000.

2 VISCOSITY MEASUREMENTS

Thickening effects are obtained when the two polymers are put together. As it has been observed for associating polymers, the viscosity increases sharply above a certain critical concentration (around 10 g/l for PEO-ADAM 20 000) 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 ß-CD are higher than $1/K_c$, that is for PEO concentrations higher than 4.5 g/l in the case of PEO-ADAM 20 000. On the other hand, the probability to link the two terminal groups of a PEO chain to two different ß-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 K_c values has been studied on PEO 6000 grafted with the three different groups whose complexation constants are ranging from 26 to 3200 $1M^{-1}$. For instance, in mixture with ß-CD/EP, weight ratio 3/2 and PEO concentration 30 g/l, the specific viscosities are 1.15, 4 and 29 times higher than the specific viscosity of the same mixture containing unmodified PEO, respectively for PEO-N1, PEO-N2 and PEO-ADAM. Better associating properties are obtained with PEO bearing adamantyl end groups.

The influence of the PEO chain length has been studied using three different molecular weights 6000, 20 000 and 35 000 of PEO-ADAM. The specific viscosities of their mixtures with ß-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-ADAM over mixtures with PEO are reported on Figure 1. The higher viscosity enhancement is obtained for PEO 20 000 and the enhancement is much lower for PEO 35 000 than for PEO 6000. Obviously, there is an optimum of the thickening properties for PEO molecular weights around 20 000, resulting from the occurrence 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 1) are qualitatively comparable (around 80%) for the 3 PEO molecular weights in the concentration range 10-30 g/l.
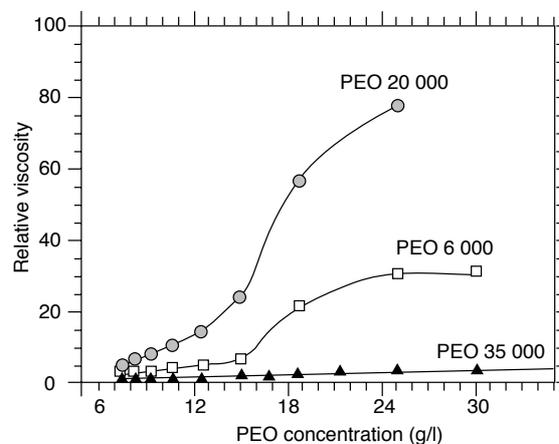

Figure 1

Influence of the PEO molecular weights. Relative viscosities are viscosity ratio of mixture (3/2 w/w) ß-CD/EP and PEO-ADAM over the equivalent mixtures with unmodified PEO.

One can notice on Figure 1 that the relative viscosities seem to reach plateau values at high PEO concentrations for PEO 6000 and 20 000. The shear rates influence has been studied in the range 0.01-10 s^{-1} for the more viscous samples and no noticeable variations of the viscosities have been observed. Thus non-newtonian behavior of the poly-molecular aggregates do not seem to be at the origin of this phenomenon. The saturation of the viscosities could rather be interpreted as a levelling at high concentration of the sizes of the aggregates. On the other hand, unmodified PEO and ß-CD/EP polymers experiment repulsive interactions since they form two phase systems at high concentrations [6].

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 ß-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 dependent 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 20 000. No network formation has been observed and the limiting growth of the polymolecular aggregates has been attributed to the repulsive interactions of PEO and ß-CD/EP polymers.

REFERENCES

1 Glass J.E. (1996), Hydrophilic polymers: performance with environmental acceptability. *Advances in Chemistry Series* 248, American Chemical Society, Washington DC.

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

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

4 Amiel C. and B. Sebille (1996), *Proceedings of the 8th Cyclodextrin Conference,* Kluwer Academic Publishers, 107-113.

5 Pitchumani K. and M. Vellayappan (1992), Complex formation of nitrobenzoic acids and some naphthalene derivatives with ß-cyclodextrin. *Journal of Inclusion Phenomena and Molecular Recognition in Chemistry,* **14,** 157-162.

6 Ekberg B., B. Sellergen, L. Olsson and K. Mosbach (1989), *Carbonhydrate Polymers,* **10,** 183.