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Synthesis, characterization and associative properties of triblock and diblock perfluorinated poly(acrylamide)s

Pierre Lebreton[1], Bernard Boutevin[1], Philippe Gramain[1], Jean-Marc Corpart[2]

[1] Laboratoire de Chimie Macromoleculaire, UPRESA 5076, Ecole Nationale Supérieure
de Chimie de Montpellier, 8 Rue de l'Ecole Normale, F-34296 Montpellier Cedex 05,
France
[2] Elf-Atochem, Centre d'Application de Levallois, 95 Rue Danton, B.P. 108,
F-92303 Levallois-Perret Cedex, France

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Summary

A triblock perfluorinated poly(acrylamide) was produced by polymerization of acrylamide at 82 °C in acetonitrile using a difunctional azo-derivative initiator bearing fluorinated groups. The presence of triblock structures was revealed by GPC analyses by changing the nature of the solvent. Fractionation of a poly(acrylamide) sample allowed us to isolate the triblock fractions from the diblock ones. Polymerization with a small amount of initiator led to a sample with few triblock structures compared to a polymerization with a large amount of initiator. It can be concluded from this that acrylamide rather gives disproportionation according to the literature and that triblock formation comes from primary radical termination.

Introduction

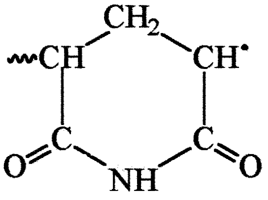
One of the most important type of associative thickeners is hydrophobically modified poly(oxyethylene). These thickeners can be synthesized from poly(oxyethylene), isocyanates and fatty alcohols (1),(2),(3),(4). Then for example octadecyl isocyanate is reacted with poly(oxyethylene) (POE) of varying molecular weight. In a second synthesis, excess isophorone diisocyanate is reacted with POE to prepare an isocyanato functional precursor, followed by the reaction of the last isocyanate group with nonylphenol (5). A two step procedure is also used with alcohol (6): 1) preparation of *n*-dodecyl *p*-toluene sulfonate (DPS) by reacting *p*-toluenesulfonyl chloride on a 1-alcohol in the presence of pyridine, according to a classical procedure 2) reaction between DPS and α,ω-dihydroxylated PEO previously metallated by potassium diphenylmethane.

Our aim was to synthesize an hydrophobically-modified poly(acrylamide) with a triblock structure analogous to «HEUR» (Hydrophobically Ethoxy Urethane), that is two hydrophobic segments located at each end of the hydrophilic polymer chain. For that purpose, acrylamide was polymerized in acetonitrile in the presence of a difunctional azo-derivative initiator bearing two hydrophobic groups, that we had synthesized previously.

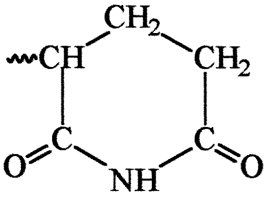
The literature mentions one article dealing with a difunctional azo-initiator containing two poly(ethyleneglycol) blocks used in the polymerization of acrylamide with Ce(IV). The acrylamide-(ethyleneglycol) block copolymers obtained, with labile azo linkages in the main chain, were used to induce the radical polymerization of acrylonitrile resulting in the formation of multiblock copolymers (7). Macroinitiators can also be used in multi-mode polymerization (8).

The bimolecular termination mode is an important factor because it determines for a large part the final functionality of the polymer. Termination by combination ensures two initiator fragments per polymer molecule whereas termination by disproportionation only gives one initiator fragment per polymer molecule. Only few studies have tried to determine the extent of termination by combination for acrylamide monomer. For example, Venkatarao et al. (9) have studied the polymerization of acrylamide in water photosensitized by uranyl ions. The polymer was fractionated and the experimental integral and differential distribution curves were drawn. The theoritical distribution function was derived from the kinetics of photopolymerization. The theoritical and experimental molecular weight distributions were compared: they did not deviate very much from each other which proved that the proposed mechanism was correct and that termination occurs mainly by disproportionation. The same conclusion was made by Suen et al. for the polymerization of acrylamide in water at 80 °C with ammonium persulfate as initiator (10). They determined the residual unsaturation in two poly(acrylamide) samples by either of two methods: 1) the bromate-bromide iodine number determination 2) a coulometric method developed by E.W. Hobart in which the sample is oxidized by permanganate, followed by coulometric titration of the excess of permanganate with a sensitivity of about 0,002%. It was concluded that the residual unsaturation in poly(acrylamide) is due to the terminal double bond and that the termination step of polymerization of acrylamide at 82 °C occurs to a large extent through disproportionation. Mitra et al. (11) described a new method to estimate carboxyl and sulfoxy endgroups in acrylamide polymer, known as reverse dye partition technique. The estimated numbers of endgroups in the polymers were in agreement with the existing free radical mechanism of initiation of polymerization. Particularly, the results of polymerization with $KMnO_4$/oxalic acid or lactic acid or citric acid system supported the idea that the termination of polymerization of acrylamide monomer occurs mainly by disproportination.

It is known that poly(acrylamide) itself slowly undergoes imidization in aqueous solution and this fact has been used to account for the «after effect» observed in the photochemically initiated polymerization of acrylamide, the formation of a cyclic imide with structure I at the radical end of a growing polymeric chain being postulated for that purpose (12). Clearly, radical chains having such glutarimidyl groups could undergo bimolecular termination by hydrogen transfer, in which case polymers having end groups with structures II and III would be formed, and enolisation of III would produce the very stable aromatic heterocyclic system IV.



I



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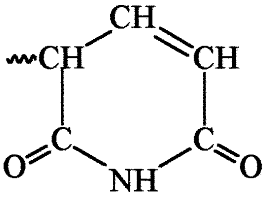

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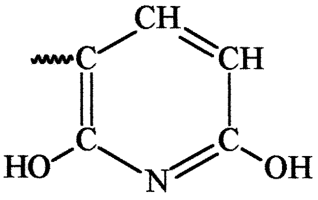


IV

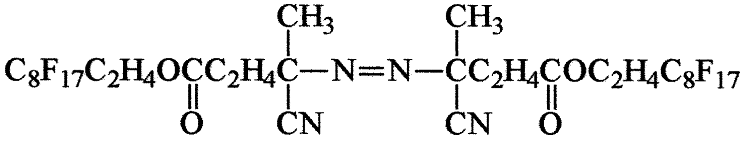
Although considerations of this kind may provide some support for the assumed termination mechanism, conclusive evidence for it is still lacking.

Since acrylamide is rather known to undergo disproportionation, it should be impossible to obtain a telechelic structure by dead-end polymerization. But it must be noticed that when high initiator concentrations and rather low monomer concentrations are employed, primary radical termination must be taken into account (13). This termination consists in a combination reaction between a primary radical coming from the initiator decomposition and a growing radical. Then, although methyl methacrylate undergoes 33% disproportionation, telechelic structures could have been obtained because the reaction conditions favoured primary radical termination (14).

In this work, we have prepared poly(acrylamide) samples with fluorinated end blocks. Two reaction conditions were chosen: low initiator and high initiator concentrations. The presence of triblock structures was revealed by gel permeation chromatography analyses in combination with rheological studies.

Results and discussion

Acrylamide was polymerized at 82 °C with a difunctional perfluorinated azonitrile initiator derived from 4,4'-azobis(4-cyanopentanoïc acid) (ACPA) (V). Modification of ACPA with fluorinated groups have already been done in our laboratory, by using another procedure (15).



$$C_8F_{17}C_2H_4O\underset{\overset{\|}{O}}{C}C_2H_4\overset{CH_3}{\underset{CN}{C}}-N=N-\overset{CH_3}{\underset{CN}{C}}C_2H_4\underset{\overset{\|}{O}}{C}OC_2H_4C_8F_{17}$$

V

Initiator synthesis is an esterification between ACPA and *1H, 1H, 2H, 2H* 2-perfluorooctyl 1-decanol with a catalytic system composed of dicyclohexylcarbodiimide and dimethylaminopyridine. The yield is around 70%. The decomposition rate constant was determined at 82 °C by thermal gravimetric analysis: $kd=2,33.10^{-4}\ s^{-1}$ with a half-time decay equal to 50 min.

Acetonitrile was chosen as the reaction medium due to its high boiling point (82 °C) and its presumed low transfer constant. The polymerization therefore proceeded heterogeneously due to the insolubility of poly(acrylamide) (see mechanism in fig. 1).

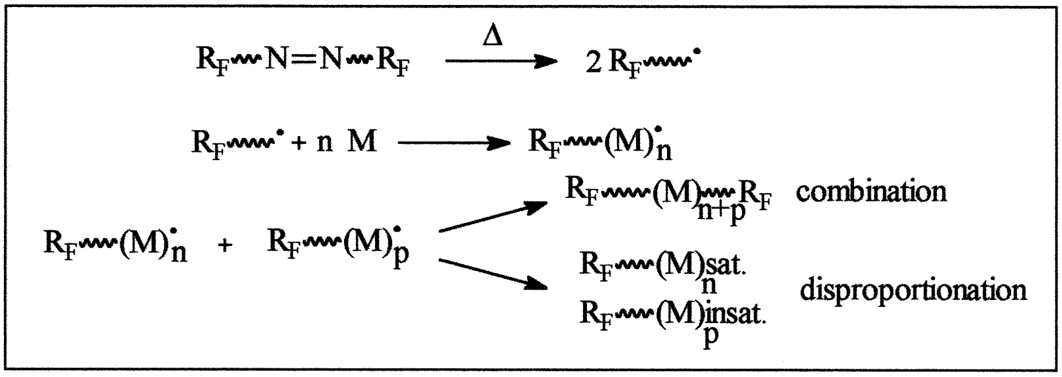


Fig.1 : Mechanism of polymerization

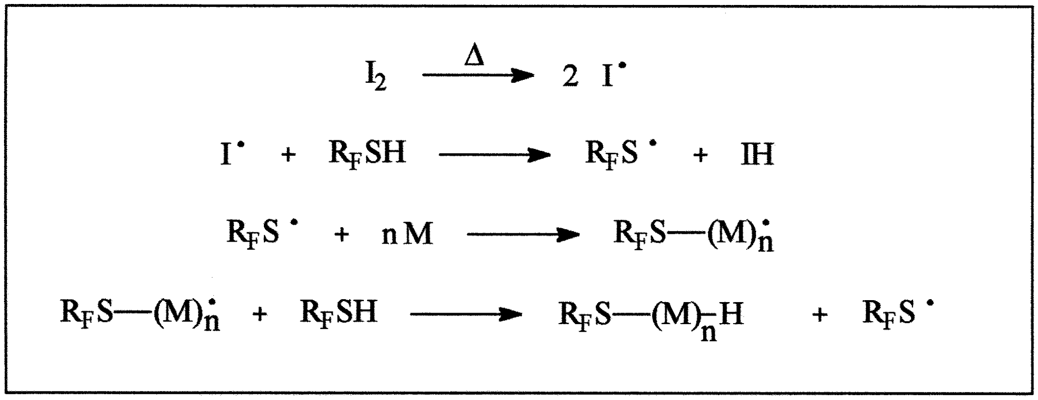


Fig.2 : Mechanism of telomerization.

	% initiator	time min	α (%)	%F	f apparent	$\overline{Mw}$, $\overline{Mn}$, I
Polymerization						
P_1	0,05%	40	54	0,09	0.15	127 000 53 900 2,3
P_2	7,00%	20	84	3,84	1.37	30 100 11 600 2,6
Telomerization						
T_1 $R=[R_FSH]/[AM]$ $=0,0062$	0,20% (AIBN)	6	<6	1,80	0.76	24 600 13 600 1,8

Table 1 : Reaction conditions and results for both polymerization and telomerization of acrylamide at 82 °C - α=conversion determinated by IR-TF-GPC results based on poly(oxyethylene) standarts - apparent functionnality (f)=$\overline{Mn} \times \%F/19 \times 17$

In order to make comparison with polymerization, we prepared a perfluorinated poly(acrylamide) with a diblock structure by telomerization of acrylamide with a perfluorinated thiol ($C_8F_{17}C_2H_4SH$) (see mechanism in fig.2) according to Mouanda (16).

The conditions and the results of both polymerization and telomerization of acrylamide at 82 °C are summarized in table 1. Polymerization is very fast and for example with 7% initiator it is almost completed within 20 min whereas the half-time decay of the initiator is only 50 min. We are not, then, in the typical reaction conditions known as dead-end-polymerization. The polymer products are soluble in mixture water/acetonitrile 70/30. Polymerization was not performed in such a solvent since initiator was not soluble even at 80°C.

The three perfluorinated poly(acrylamide) samples were analysed by gel permeation chromatography using three columns from Tosohaas G2500 PW_{XL}, G3000 PW_{XL} and G4000 PW_{XL}. Analyses were conducted in three distinct carrier solvent: water, water/acetonitrile 90/10 (v/v) and water/acetonitrile 70/30 (v/v). The elution of the polymer was strongly influenced by the composition of the carrier solvent, especially for the sample obtained with 7% initiator (P_2, fig. 3). In water, the elution chromatogram shows three peaks. The first two peaks appear at very high molecular weights around 10^5

and 10^6 whereas the last one appears at lower molecular weights around 2.10^4. With addition of 10% acetonitrile in the carrier solvent, the excluded fraction begins to disappear. Finally, with 30% of added acetonitrile, it only remains the last elution peak connected with normal polydispersity (2,6) and low molecular weight ($\overline{Mw}$ = 30 100). We believe this elution dependency on the solvent composition to be consistent with the presence of associative structures in the P_2 poly(acrylamide) sample. Hydrophobically-modified water-soluble polymers are effectively well-known to associate in water, thus forming, even at low concentrations, aggregates of high hydrodynamic volumes. Addition of an appropriate organic solvent in water makes the hydrophobic segments more soluble in the medium thus dissociating aggregates at the same time (17) (18). This explains the results found in going from water to water/acetonitrile elution. In water, trimodal elution corresponds to separate elution of aggregated and non-aggregated molecules, owing to large differencies in their hydrodynamic volumes. With 10% acetonitrile, aggregates tend to disappear but are still largely present and finally with 30% acetonitrile aggregates are no more detected. Here aggregates must be formed by the association of the triblock structures of the type R_F-PAM-R_F.

The presence of triblock structure are not so clear in P_1 compared to P_2 (chromatograms not given here). But some exclusion phenomena observed in water elution that disappear with 30% acetonitrile may indicate the presence of a small amount of associative structure. T_1 elution (not given here) can be compared to F_3 elution: there is no significant change on going from water to water/acetonitrile elution as it could be expected from the non-associative behaviour of its diblock structure.

In order to confirm the associative nature of the triblock structure we performed a rheological study on the carrimed CSL 100 rheometer. P_1, P_2 and T_1 were analysed in 8% aqueous solutions and the rheological data (viscosity vs shear rate) are shown in graph. 1. We can notice that the P_1 and P_2 solutions are viscous but not the T_1 solution.

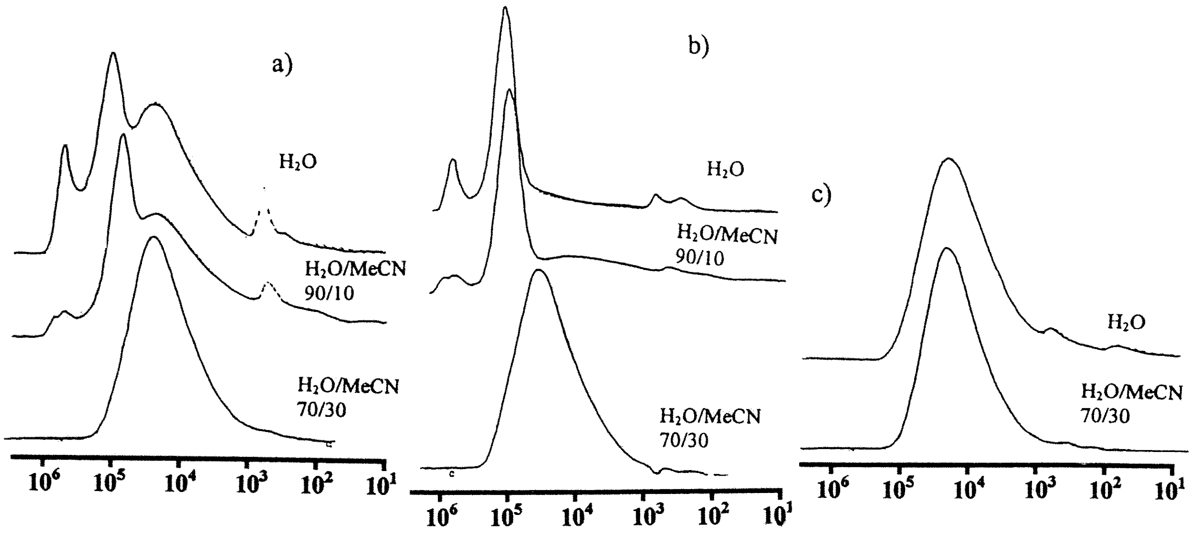
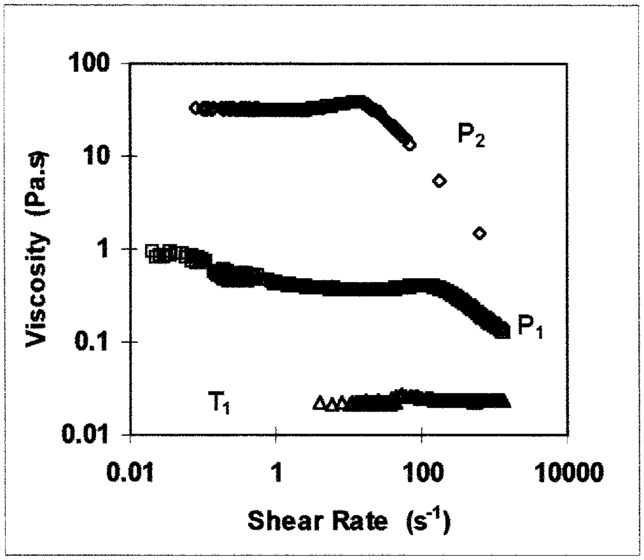
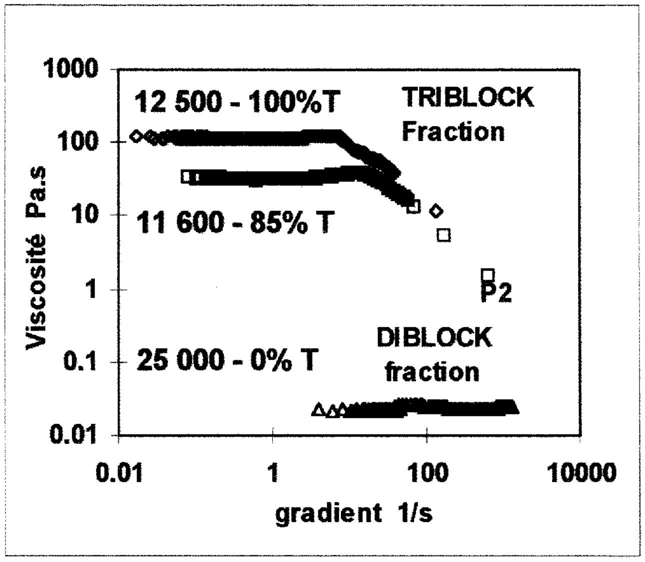


Fig.3 : GPC analyses of P_2 (a) and two of its fractions : F_1 (triblock) (b) and F_3 (diblock) (c)



Graph 1 : Rheological study - Viscosity as a function of shear rate for three poly(acrylamide) samples in aqueous solution - Cp=8%



Graph 2 : Rheological study - Viscosity as a function of shear rate for P_2 sample and its triblock and diblock fractions in aqueous solutions - Cp=8% - $\overline{Mn}$ and % triblock are given

Fraction	weight (g)	%F	$\overline{Mn}$ (GPC)	apparent functionality	nature
F_1	3.8	5.1	12 500	1.97	triblock
F_2	0.14	1.6	14 500	0.72	triblock + diblock
F_3	0.32	0.3	25 000	0.23	diblock
F_4	0.26	1.0	5 600	0.17	diblock

Table 2 : Fractionation results of P_2 (%F=3.8) - weight fractionated : 5,6 g - Mn (GPC) is determinated in non associative elution conditions

P_2 shows typical associative behavior with a newtonian behaviour over a wide range of shear rates, shear thickening in the range 10 s^{-1} and finally shear thinning. T_1 exhibits a newtonian behaviour over the entire shear rate range. A diblock molecule is not then an appropriate thickening agent. P_1 solution is less associative than P_2 solution (see the viscosity value at zero gradient: 0,9 Pa.s against 33 Pa.s). Two factors can explain that : first of all, P_1 sample contains less associative structures than P_2 as it can be deduced from the comparison of their apparent functionality (table 1). Secondly, molecular weight is known to influence strongly the viscosifying abilities: for example, for hydrophobically modified PEO there is a maximum of viscosity for molecular weight around 13 000 g/mol and it is related to the hydrophilic/lypophilic balance (19).

At last P_2 sample was fractionated into four fractions by a very simple procedure. Acetonitrile is slowly added under continuous stirring, into a 6% concentrated P_2 solution in a 70/30 water/acetonitrile solvent until appearance of a cloudiness. The solution is then gently warmed at 50 °C until it becomes clear and slowly cooled to 5 °C. After one or two days at 5 °C, a phase separation occurs. The lower viscous phase is separated carefully from the upper phase and then reprecipitated in acetonitrile after dilution with water. The clear non-viscous upper phase is another time submitted to fractionation until no more phase separation occurs. Then the last fraction is concentrated and precipitated in acetonitrile. Results of the P_2 fractionation are shown in table 2. There are four fractions with varying fluorine contents and molecular weights. Each nature of the fractions could be determined by their apparent functionality or again by their elution dependency in GPC analysis. A typical example can be found in fig.3 for the F_1 and F_3 fractions. They are respectively pure in triblock and diblock as it can be seen from the single peak found in water. The elution of the F_1 fraction (triblock) clearly depends on the acetonitrile content in the solvent whereas the elution of the F_3 fraction (diblock) is not changed by the presence of acetonitrile. According to the weight of each fraction, P_2 sample contains 84% of triblock structures. The graph 2 confirms the associative nature of the triblock fraction and the non-associative nature of the diblock one.

In conclusion we showed that triblock perfluorinated poly(acrylamide) can be obtained by polymerization with an appropriate initiator provided its concentration is not too low. Fractionation of the polymerization product allowed us to confirm the presence of both diblock and triblock structures by means of GPC analyses and rheological studies. Triblock poly(acrylamide) can be used as additive in fire-fighting aqueous formulation (20) or as associative thickener in painting formulations (21).

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