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ANIONIC POLYMERIZATION AND COPOLYMERIZATION OF MACROMONOMERS: KINETICS, STRUCTURE CONTROL

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Abstract: The present paper discusses the ability of macromonomers to undergo polymerization and copolymerization with acrylic and vinylic monomers. These macromonomers have been synthesized by classical deactivation reactions. Special interest was devoted to macromonomers fitted with polymerizable methylmethacrylate end-groups. The anionic homopolymerization of ω-methacryloyloxy-polystyrene macromonomers was studied in detail and the influence of the molar mass of the macromonomer on the apparent propagation constant was determined. The anionic homopolymerization of ω-methacryloyloxy poly(ethylene oxide) macro-monomers was also examined. In both cases, lithium chloride has to be added in order to reach a better control of the reaction. The dilute solution properties of these polystyrene polymacromonomers have been studied. Some preliminary attempts to apply that anionic homopolymerization of macromonomers to the preparation of "dumbbell" and "palmtree" polymers were presented.

INTRODUCTION

Macromonomers are defined as polymers carrying a polymerizable entity at one or two chain ends (Refs. 1- 3). Their molar masses typically cover a range of 1000 to 20 000 g/mol. The radical copolymerization of macromonomers with low molar mass polymerizable compounds provides an easy access to graft copolymers and was therefore applied to a large number of systems (Ref. 3). This method of preparation is now preferred to the classic "grafting on" or "grafting from" procedures (Ref. 4). The homopolymerization of macromonomers represents an original way to access highly compact branched species where each monomer unit in the backbone carries a graft. The ability of macromonomers to homopolymerize (or to copolymerize) can be questioned for several reasons:

- their molar mass is usually in the order of 10^3 to 2.10^4 g/mol thus the molar concentration of polymerizable units is rather low, with the expected consequences on the polymerization

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yields. This is specially the case if one considers the classical radical polymerization characterized by short life time of the active sites.

- the lower accessibility i.e. the presence of a polymer chain attached to the polymerizable entity limits the mobility of the polymerizable unit and may influence its intrinsic reactivity as compared to the low molar compound exhibiting the same type of unsaturation.
- as pointed out earlier, transfer reactions may occur during the growing process. This has dramatic consequences leading in some cases to irreversible gel formation during the process.

This is confirmed by the low polymerization yields and the low polymerization degrees obtained for the free radical homopolymerization of macromonomers (Refs. 5,6). Some attempts by Group Transfer Polymerization (GTP) have to be mentioned (Ref. 7). The case of anionic polymerization may be more favorable as the active sites are basically living for long times. The anionic homopolymerization of polystyrene (PS) macromonomers, fitted with polymerizable styrene units, was studied a few years ago. This homopolymerization could be kept under control and good yields were obtained (Ref. 8). On the contrary, the anionic homopolymerization of PS macromonomers fitted with polymerizable methylmethacrylate end groups was not very successful (Ref. 9).

The first part of the present work discusses a systematic study of the anionic polymerization of ω-methacryloyloxy PS and poly(ethylene oxide) (PEO) macromonomers with the aim of determining the appropriate conditions to control the polymerization and of determining the apparent propagation constant of the polymerizable methylmethacrylate unit. Thus, the solution properties of the PS polymacromonomers will be presented and compared to those of polymers of other architectures. The anionic block copolymerization of macromonomers with low molar mass polymerizable compounds enables the preparation of well-defined architectures such as "dumbbell" or "palmtree" polymers. This point will be briefly discussed in the final section.

EXPERIMENTAL

The polystyrene macromonomers were prepared by induced ionic deactivation according to a method published earlier in the literature (Ref. 8). PEO with end standing methylmethacrylate units were prepared either by modification of the chain end of monofunctional commercial PEO followed by addition of methacryloyl chloride or by direct deactivation of living monofunctional PEOs (Ref. 8). These different samples were submitted to a detailed characterization to confirm the expected structure.

The polymacromonomers were prepared by polymerization of the macromonomer as indicated. The sample was freeze-dried in order to remove the remaining protonic impurities.The homopolymerization was then carried out in THF (free of any impurities) at low temperatures generally in the presence of Lithium Chloride (LiCl), the ratio [LiCl]/[LE] (Living Ends) being equal to 5. 1,1-Diphenyl-3-methyl-pentyllithium (DPMPLi) was used as the initiator, the amount of DPMPLi depending upon the desired polymerization degree and the concentration of the initiator. The macromonomer solution was added rapidly to the THF solution containing the initiator. The coloration of the reaction mixture vanished immediately confirming the consumption of the initiator. The reaction mixture was then kept at constant temperature. At given times, samples were taken out for purpose of characterization by SEC/LS. Thus, both the conversion and the molar masses can be obtained.

"Palmtree" and "Dumbbell" polymers were prepared on the same way, the monofunctional initiator being replaced by a mono-or bifunctional living PS precursor chain.

The solution properties, in the dilute a semi dilute regime, were examined by static or dynamic light scattering and neutron scattering according to well established procedures.

RESULTS AND DISCUSSIONS

Homopolymerization

Polystyrene polymacromonomers

Earlier experiments (Ref. 9) have shown that the anionic homopolymerization of ω -methacryloyloxy PS macromonomers can be conducted to high yields. A good control of the polymerization degrees could not be achieved. This result may be attributed to an uncontrolled polymerization of the methylmethacrylate group. One has also to be aware of the fact that the stability of the methylmethacrylate active sites is questionable for long reaction times. Well defined PS polymacromonomers, characterized by a backbone and grafts of different chemical nature may yet be of interest. This is why we have further developed the anionic homopolymerization of ω-methacryloyloxy PS macromonomers.

It is well known, that the polymerization of MMA is affected by the presence of various additives. Teyssie et al. (Ref. 10) have shown, a few years ago, that the introduction of LiCl improves the molar mass distributions and lowers the nucleophilicity of the active sites preventing transfer and termination reactions.

Macromonomers of various molar masses have been submitted to anionic homopolymerization, in the presence of LiCl or not. From the results gathered on Tab. 1 following remarks can be made :

- Provided appropriate initiators are used, well defined PS polymacromonomers can be obtained. The polymerization yields, determined by SEC, are always quantitative and that, even in the presence of LiCl at low temperature (-60 °C) where the propagation reaction is expected to be slow. Contrary to the free radical homopolymerization, where the homopolymerization yields are never quantitative, here the macromonomer is incorporated almost quantitatively. These samples can be used without further purifications for the study of the solution properties.

- In a polymacromonomer each unit of the main chain carries a graft. Polymacromonomers are also very compact species exhibiting a very high segment density within the coil. As a consequence, their hydrodynamic volume is very small as compared to the linear homologous. Thus classical SEC based on calibration with linear samples can not be applied properly. These samples were also characterized by SEC on line with light scattering.
- The measured homopolymerization degrees (DP_n) are in good agreement with the calculated values at least in a range of DP_n ratios from 10 to 50. From the shape of the SEC diagrams one can also estimate the polymolecularity which was found to be low.

Tab. 1. Homopolymerization results

Sample	M_w a) Macro.	DP_n b)	React.temp. React. Time	M_w a) PM	DP_n c)	Yields w %
209	1350	10	- 40 °C /2h (d)	17000	12	93
210	1350	40	- 40 °C /2h (d)	64 000	48	96
248	3400	10	- 60 °C /2h (d)	31 000	9	97
206	4400	10	- 60°C / 5h no LiCl	44 000	10	96
221	6500	10	40 °C /2h (d)	63 000	10	93
225	10900	10	- 40 °C /2h (d)	97 000	9	97

a) M_w Molar mass of the polymacromonomer (PM) obtained by SEC /LS coupling taking into account the measured value of (dn/dc).

b) Polymerization degrees calculated from the ratio of the concentration of polymerizable units to initiator concentration,

c) results obtained

d) Ratio [LiCl] / [LE] equal to 5

Kinetic studies of the homopolymerization of PS macromonomers

The kinetics of the free radical copolymerization of macromonomers has been examined for various systems (Ref. 3). Only few work has been done until now in the domain of anionic copolymerization of macromonomers (Ref. 11-12). The kinetics of the anionic homopolymerization has never been examined.

The homopolymerization experiments previously described have drawn to the conclusion, that the homopolymerization yields are not only dependent on the polymerization time or temperature, they are also affected by the presence of LiCl. The major goal of this work was to determine whether or not, the presence of a polymer chain attached to the polymerizable methylmethacrylate entity affects its propagation constant. We have examined in detail this reaction. Different macromonomers were submitted to anionic polymerization. The conditions are indicated in Tab. 2. At given reaction times samples were taken out and characterized by SEC. By integration of the different areas of the SEC diagrams (Fig. 1), it is possible to calculate the concentration of the different species in presence and to plot the logarithm of the quotient Q where Q is equal to $[M]_0$ / [M] versus time. The kinetics for a first order polymerization follows the equation given below:

$$\ln(\frac{[M]_o}{[M]}) = kp \cdot [A^-] \cdot t$$

In this case the concentration of [M] and $[M]_0$ can be calculated by the integral of the polymacromonomer and the macromonomer SEC peaks such as:

$$[\mathrm{M}]_0 = \int(\text{Polymacromonomer}) + \int(\text{Macromonomer})$$

$$[\mathrm{M}] = \int(\text{Macromonomer})$$

This leads to the resulting equation:

$$\ln(\mathrm{Q}) = \ln\left[\frac{\int(\text{Polymacromonomer}) + \int(\text{Macromonomer})}{\int(\text{Macromonomer})}\right] = \mathrm{kp} \cdot \left[\mathrm{A}^-\right] \cdot \mathrm{t}$$

Where [A ⁻], the concentration of active sites in the reaction medium, is constant and kp is the apparent propagation constant of the methylmethacrylate unit.

The apparent rate constant of propagation can be calculated by the ratio of the slope of the resulting linear curve to the known concentration of the anionic species.

Fig 2 shows the first order plot of the macromonomer conversion versus time.

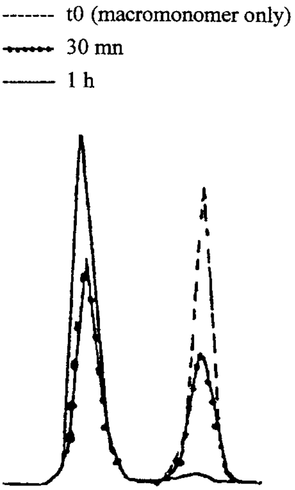

Fig. 1.Evolution of the SEC diagrams for the macromonomer and the polymacromonomer

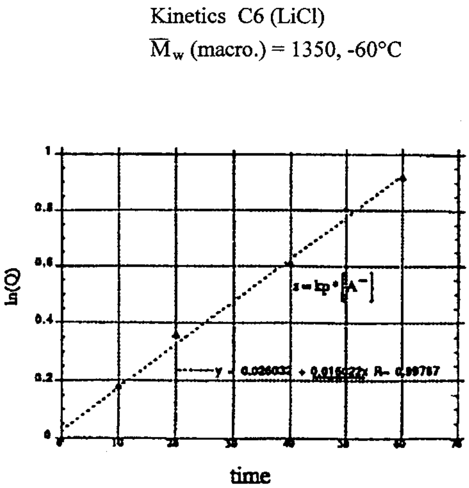

Fig. 2. Plot of the conversion in polymacromonomer versus time (in mn)

The experimental results are gathered on Tab. 2. and call for a few comments: as a first assumption we consider that the anionic polymerization of these macromonomers follows the ideal case of anionic polymerization: no transfer, no termination. The propagation constants we measure are apparent constants. We will not take into account the existence of various active species in the reaction medium.

-As mentioned ealier, the presence of LiCl affects the values of the propagation constant (k_p) for the monomer and for the macromonomer.

- As expected, an increase of the reaction temperature results in an increase of k_p.

-The most important result concerns the effect of the molar mass of the macromonomer: for a given temperature, the value of k_p decreases with increasing molar mass. It is also now established, that in the anionic homopolymerization of such macromonomers, the molar mass of the macromonomer determines the value of k_p of the polymerizable unit.

Tab. 2. Determination of the apparent propagation constants

Kinetics	Molar mass	Temp.(°C)	$k_p.10^{-3}$ with LiCl ($mol.L^{-1}.s^{-1}$)	$k_p.10^{-3}$ without LiCl ($mol.L^{-1}.s^{-1}$)
(9)	MMA (1)	- 65	10 400	20 000
C5, C6	1350	- 60	310	-(2)
C7, C8	1350	- 40	-	1220
C9, C10	3400	- 60	180	710
C11, C12	3400	- 40	300	900
C13, C14	4400	- 60	100	-
C15, C16	4400	- 40	190	520
C17, C18	10 000	- 60	8	-
C19, C20	10 000	- 40	20	-

(1)Monomer methylmethacrylate, (Ref. 13), (2)too rapid, difficult to be calculated

Poly(ethylene oxide) macromonomers

The case of homopolymerization of PEO macromonomers fitted at the chain end with polymerizable methylmethacrylate unit was rather different. A first limitation was the difficulty to obtain a good purification of the macromonomer without uncontrolled polymerization of that macromonomer. Furthermore, these PEO macromonomers have a strong tendency to crystallize specially at low temperature and a good control of the anionic polymerization of methylmethacrylates implies low temperatures. This is why the anionic homopolymerization of ω-methacryloyloxy PEO macromonomers was not very successful. Some results are gathered on table 3.

Tab. 3. Characterization data of PEO polymacromonomers

No.	M_w (a)	React. cond. (b)	DP_n cal.	M_n cal (c)	M_w mes. (d)	DP_n mes (d)	Yield %
337	5000	- 15°C / 1/2 h	15	75 000	61 000	12	77
356	1900	- 30 °C /1/2h	10	19 000	26 000	14	50
357	1900	- 30 °C /1/2h	20	38 000	39 000	20	50

a) M_w (g/mol) obtained by SEC in water (PEO cal.)

b) reaction conditions: temp/time. The ratio [LiCl]/[LE] ends is equal to 5 in all cases

Initiator: *sec*-BuLi/ 1,1-diphenylethylene in THF solution

c) Molar mass calculated from the ratio macromonomer to initiator, d) results obtained

Well-defined amphiphilic polymacromonomers could not be obtained by this way. Further work is now under progress to examine the effect of other additives that could enable a controlled polymerization of the methylmethacrylate unit at room temperature where the crystallization of the PEO chain does not occur.

Solution properties

Before studying the solution properties of these PS polymacromonomers containing a PMMA backbone we have first examined the dilute and semi dilute solution properties of PS polymacromonomers, where backbone and grafts as constituted of PS. In this case the incompatibility between grafts and backbone does not exist. Some results are gathered on Tab. 4. As the dimensions of these species are not accessible by light scattering we have carried out neutron scattering experiments in a deuterated solvent. It was found that the values of radii of gyration are much lower than those of linear chains. The limiting viscosity numbers were also smaller. The hydrodynamic dimensions of these polymacromonomers have been measured by dynamic light scattering. The hydrodynamic radii were determined and were found to be much smaller for polymacromonomers than for linear chains of the same molar mass. The value of the ρ parameter is comparable to that measured for star-shaped polymers exhibiting the same functionality.

All these parameters have been determined in dilute solutions because the macromolecules are only weakly perturbed by the intramolecular interactions. The region of higher concentrations is also of interest and the question arises how these branched macromolecules interpenetrate as compared to linear samples or to other branched species.This behavior is very complexe as in semi-dilute solutions strong thermodynamic and hydrodynamic interactions coexist. The osmotic modulus provids an easy access to these parameters. The values obtained were compared to those found for other architectures. These results will be discussed in a forthcoming paper (Ref. 14). Further work is now under progress on the solution properties of PS macromonomers fitted with a PMMA backbone.

Tab. 4. Characterization data of polymacromonomers

PM	M_n	M_{wLS}	[η]	[η]	$D.10^7$	$D.10^7$	R_g	R_h	ρ
	Macro.	Poly M	PM,	Lin.	QELS	cal.	SANS	QELS	
			THF	THF	tol.	tol	tol.(nm)	tol.(nm)	
1	4000	102 000	8.5	44.8	6.5	4.33	7.8	6.7	1.16
2	10 000	119 000	12.7	50.0	5.7	3.96	8.4	7.9	1.06

[η] limiting viscosity numbers

The ρ parameter corresponds to the ratio of the geometrical defined radius of gyration (R_g) and to the hydrodynamic radius (R_h) which is defined through the Stockes-Einstein relation and D ($cm^2.s^{-1}$) corresponds to the translational diffusion coefficient measured in toluene.

$$\rho = R_g / R_h \quad \text{and} \quad R_h = kT / (6\pi\eta_0 D),$$

Anionic copolymerization of macromonomers

"Dumbbell" polymers containing a central PS block linking two branched PEO's have been prepared recently (Ref. 15) and were shown to exhibit typical properties of amphiphiles.

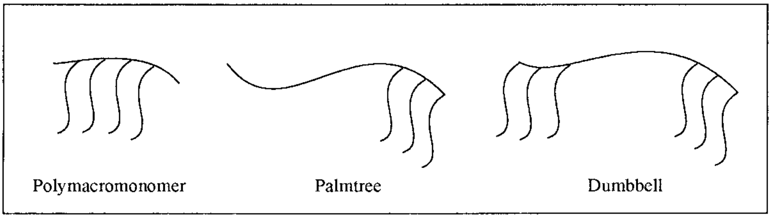

Fig.3. Schematic representation of the structures of branched polymers based on macromonomers

They were prepared from triblock copolymers containing terminal hydroxylated segments. We have developed another approach to prepare such "dumbbell" species or "palmtree" polymers (Fig. 3) based on anionic homopolymerization of macromonomers. The anionic polymerization of a monofunctional or bifunctional living polystyrene chain was conducted first. The carbanionic chain ends served thus as initiator for the anionic polymerization of the ω-methacryloyloxy PS macromonomer. An example is given on tab. 5. In spite of the fact that the molar mass distribution of the precursor chain is rather large, the molar mass of this "palmtree" polymer corresponds to the expected value. The calculated value for the DP_n of the polymacromonomer (DP_n =5) is close to the measured value.

Tab. 5. Characterization data of a "palmtree" polymer obtained upon anionic copolymerization with macromonomers

Sample	M_n(1)	M_w(1)	M_w/M_n	M_n (2)	M_w	M_w/M_n
Macro.	2300	2500	1.1	-	-	-
Precursor	10 500	16 400	1.56	12 000	16500	1.38
Palmtree	15 700	21 400	1.36	23 100	25400	1.10

1) Molar masses obtained by SEC, calibration with linear PS

2) Molar masses measured by combined SEC and light scattering one line

These species were characterized from their dilute solution properties in order to confirm the expected structure. Various types of central blocks can be introduced in these polymers: PS, PMMA or even polydiene chains containing high contents of 1,4-cis units.

CONCLUSION

In this paper we demonstrate that well defined branched polymers can be obtained by controlled anionic homopolymerization of end-standing ω-(methacryloyloxy) PS macromonomers. From the kinetic study it could be concluded that the molar mass of the macromonomer chain and the presence of LiCl affect the value of k_p. These results open new perspectives in the anionic homopolymerization of other macromonomers exhibiting the same type of polymerizable end-groups. Special effort will be made to homopolymerize or copolymerize ω-methacryloyloxy PEO macromonomers with the aim of preparing well defined branched polymers exhibiting a hydrophobic backbone and water soluble grafts. Further work is also under progress to examine in detail the solution properties of these different polymacromonomers and the results will be published soon. Finally the use of supercritical fluids chromatography gives access to uniform polymers i.e. macromonomers and allows thus the synthesis of well-defined comb-shaped polymers where all the grafts have exactly the same length (Ref. 16).

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