

Figure 1. GPC curves for poly(methyl methacrylate) (A) and for poly(butyl methacrylate-*block*-methyl methacrylate-*block*-butyl methacrylate) (B): peak A, $\bar{M}_n(\text{obsd}) = 2200$, $\bar{M}_w/\bar{M}_n = 1.14$; peak B, $\bar{M}_n(\text{obsd}) = 7200$, $\bar{M}_w/\bar{M}_n = 1.21$.

Table I
Polymers by GTP with Initiators 1 and 2

expt ^a	monomer ^b (mmol)	initiator (mmol)	calcd MW	obsd ^c		<i>D</i> (= \bar{M}_w/\bar{M}_n)
				\bar{M}_n	\bar{M}_w	
1	MMA (7.5)	1 (0.68)	1390	2200	2500	1.14
2	BMA (14.6)	2 (0.33)	6110	9910	12190	1.23
3	AMA (13.5)	2 (0.33)	5200	8370	10130	1.21
4	1. MMA (4.9) 2. BMA (10.1)	1 (0.44)	4380	7200	8710	1.21
5	1. BMA (7.0) 2. MMA (7.0)	2 (0.33)	5040	8160	10360	1.27
6	1. MMA (6.0) 2. MA (12.0)	1 (0.34)	4850	7290	9550	1.31
7	1. AMA (4.5) 2. MMA (15.9)	1 (0.34)	6350	9860	12720	1.29
8	1. MMA (7.0) 2. AMA (8.0)	2 (0.33)	5080	8380	10640	1.27
9	1. AMA (4.6) 2. HEMA ^d (8.3)	1 (0.34)	6660	11340	14180	1.25

^a Catalyst: TASHF₂, 0.06 mL (0.1 M in CH₃CN). Solvent: THF, 5 mL (except to experiments 1 and 4). Yield, all quantitative. ^b AMA, allyl methacrylate, MA, methyl acrylate; (1) B block; (2) A block in ABA triblock copolymer. ^c Obtained from GPC (Waters Model 150 C) in THF by using polystyrene standards. ^d 2-(Trimethylsiloxy)ethyl methacrylate.

after stirring overnight. From the above result the product is considered to consist of ABA triblock copolymer.

The experimental data of homopolymers and ABA triblock copolymers with the difunctional initiator 1 and 2 are summarized in Table I. The degree of polymerization was controlled by the ratio of monomer to initiator. The molecular weights show narrow molecular weight distributions, typically $D (= \bar{M}_w/\bar{M}_n) = 1.1-1.3$. The experimental molecular weights of the polymers are about 50-70% higher than those of theory, which is probably due to the fact that values are calculated by a polystyrene calibration curve.

To confirm the structure of the "living" or silyl ketene acetal end group of the polymer, the oligo-PMMA was prepared with 2 as difunctional initiator. The peaks at 151.8, 95.5, 56.4, and 0.5 ppm which well correspond to those of 2 were exhibited in the ¹³C NMR spectrum of the oligomer. Hence, the B-block is constructed first as a homopolymer with two living ends followed by addition of A-blocks to give an ABA triblock copolymer.

In conclusion, this difunctional initiator system provides a very useful method for the synthesis of ABA triblock copolymers by using GTP. A more detailed description of these and other studies related to difunctional initiators will be discussed elsewhere.

Registry No. 1, 115533-61-4; 2, 56920-00-4; TASHF₂, 85248-37-9; MMA (homopolymer), 9011-14-7; BMA (homopolymer), 9003-63-8; AMA (homopolymer), 25189-05-3; (MMA)(BMA) (block copolymer), 107404-23-9; (MMA)(MA) (block copolymer), 108150-11-4; (AMA)(MMA) (block copolymer), 115533-62-5; (AMA)(HEMA) (block copolymer), 115533-63-6; dimethyl 2,4-dimethylglutarate, 2121-68-8; lithium diisopropylamide, 4111-54-0; dimethyl 2,5-dimethyladipate, 19550-58-4; chlorotrimethylsilane, 75-77-4.

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Probing of the Ion Pair Association in Model Ionomers by Excimer Fluorescence

During the last two decades, ionomers, which are polymers containing a low concentration of charged units along the chain, have received an ever increasing interest.¹ The occurrence of thermoreversible ionic cross-links in the polymer dramatically changes some of its properties and opens the way to an extended range of applications. Among other effects, the ion pair association is responsible for the limited solubility of ionomers in nonpolar solvents. In low-polarity solvents, such as THF, ionomers, as exemplified by a lightly sulfonated polystyrene (1-5 mol % sodium sulfonate), are, however, soluble and exhibit a solution behavior that strongly depends on polymer concentration.² Above a critical concentration (C^*), approximately corresponding to polymer coil overlap (C^*), there is a marked increase in reduced viscosity, while below C^* , the viscosity is significantly less than that of the starting polymer. It has been suggested that interpolymer association predominates above C^* , while intramolecular as-

sociation prevails below C^* .³ Transition from intra- to intermolecular association has also been assumed in order to explain the solution viscosity of halato-telechelic polymers (HTP),^{4,5} which have been designed as models for the more complex ionomers.⁶⁻⁸ In HTP's, the ionic groups are selectively attached at both ends of linear chains, instead of being randomly distributed along the chain like in ionomers. At very high dilution (<0.1 g dL⁻¹) in a nonpolar solvent, metal carboxylato-telechelic polybutadiene (\bar{M}_n 4600) shows a relative viscosity quite similar to that of the unneutralized precursor.⁴ The metal carboxylate ion pairs should therefore associate intramolecularly, allowing the individual chains to be independent of each other. At increasing polymer concentration, the relative viscosity increases sharply, which indicates that the end groups of different chains associate into multiplets, and lead ultimately to a tridimensional polymer network as assessed by gelation of the solution.

No direct evidence for intramolecular association at very low polymer concentration has been provided so far. In this regard, fluorometry, and especially fluorescence emission of an intrachain excimer,⁹ should be an efficient technique. Let us remind that an excimer is a complex formed between an excited and a ground-state aromatic molecule with a characteristic band in the emission spectrum. Excimer formation may be used as a spectroscopic short-range sensor, since a characteristic emission is only observed when the molecules overlap at short distances. Pyrene is a very well-suited chromophore for experiments of excimer fluorescence, due to the long lifetime of the excited singlet and the emission band of the excimer which is red-shifted ($\lambda_{\max} \sim 480$ nm) from the normal pyrene emission ($\lambda_{\max} \sim 380$ nm).⁹ Using polystyrene end capped with a pyrene group, Winnik et al. have collected interesting information on end-to-end cyclization of polystyrene in different media.¹⁰

This paper aims at reporting results concerning the association of ion pairs attached at both ends of a linear chain in a nonpolar solvent. A sample of α,ω -bis(dimethylamino)polystyrene has been purposely quaternized with formation of ionic end groups. Most of the telechelic polystyrene has been quaternized with 1-bromoethane, while a minor fraction has been quaternized with 3-(1-pyrenyl)-1-bromopropane in order to attach a pyrene unit at both ends of the chain. Mixing the unlabeled and the labeled quaternized α,ω -bis(dimethylamino)polystyrene in an appropriate ratio is expected to be an efficient tool in probing the intramolecular association of the ion pairs at very high dilution and for observing the expected transition from intra- to intermolecular association as the polymer concentration increases over C^* .

Polymer Synthesis. The living anionic polymerization of styrene was performed in THF, at -78°C , using naphthalene-lithium as a difunctional initiator. The living macrodianions were deactivated by 1-chloro-3-(dimethylamino)propane,¹¹ resulting in the expected α,ω -bis(dimethylamino)polystyrene. The molecular weight as determined by size-exclusion chromatography, in THF at 25°C , was 12 000 and the molecular weight distribution was narrow ($\bar{M}_w/\bar{M}_n \sim 1.1$). The functionality was determined by potentiometric titration of the tertiary amino groups by *p*-toluenesulfonic acid in a 9/1 benzene-methanol mixture and was found to be 1.85. The dimethylamino-telechelic polystyrene was quaternized with 1-bromoethane and 3-(1-pyrenyl)-1-bromopropane in refluxing THF for three weeks. No residual amino function could be detected by potentiometric titration with *p*-toluenesulfonic acid.

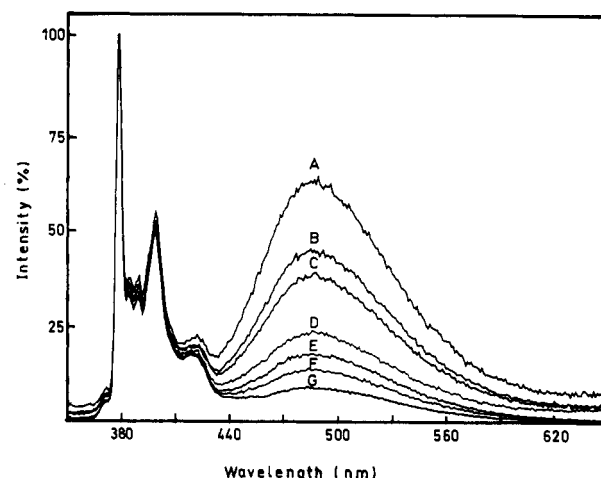


Figure 1. Emission spectra of the quaternized α,ω -bis(dimethylamino)polystyrene (\bar{M}_n 12 000) recorded at various concentrations in toluene at 25°C . The quaternary ammonium ion pairs are pyrene labeled to such an extent that [pyrene] = 5×10^{-6} mol·L⁻¹. Polymer concentrations (g·dL⁻¹): 5.8×10^{-3} (A); 6.5×10^{-2} (B); 0.1 (C); 0.3 (D); 0.5 (E); 0.65 (F), and 2.0 (G).

Fluorescence Measurements. Carefully outgassed solutions in spectrophotometric grade toluene have been excited at 346 nm and the emission intensity has been measured at 379 nm for the pyrene monomer (I_M) and at 485 nm for the excimer (I_E). Preliminary experiments have been performed in order to determine the most appropriate concentration in pyrene. The weight ratio of labeled and unlabeled polystyrene actually allows to adjust the pyrene concentration in the polymer solution. The I_E/I_M ratio has been measured in relation to pyrene concentration at a constant polymer concentration (6.5×10^{-2} g·dL⁻¹), selected in the range where solution viscosities were previously observed to be mainly independent of the ionic end groups (<0.1 g·dL⁻¹).⁴ Table I reports values of the I_E/I_M ratio for different pyrene concentrations from ca. 10^{-6} to 10^{-4} mol·L⁻¹. It appears that interchain excimer formation is favored, i.e., I_E/I_M increases, when the pyrene concentration exceeds approximately 10^{-5} mol·L⁻¹. Below that concentration, I_E/I_M does not change significantly although pyrene has been diluted six times, supporting that only intrachain associations occur. A 5×10^{-6} mol·L⁻¹ concentration of pyrene is thus appropriate, since the probability for pyrene attached to different chains to associate is negligible. Thus, at the low polymer concentration of 6.5×10^{-2} g·dL⁻¹, the ion pairs of polystyrene tend to associate intramolecularly to such an extent that the intensity emitted by the related pyrene excimer (I_E) is half that emitted by the pyrene locally excited state (I_M). The questions are now addressed whether the change in overall polymer concentration has an effect on the intramolecular formation of the excimer (i.e., I_E/I_M) and, if so, what is the meaning of that effect.

Figure 1 shows the emission spectra of solutions of the quaternized α,ω -bis(dimethylamino)polystyrene at various polymer concentrations in toluene, keeping the pyrene concentration constant at 5×10^{-6} mol·L⁻¹. Those spectra have been normalized at the maximum of emission of the locally excited state of pyrene, which is observed between 350 and 440 nm. The structureless emission band from 440 to 650 nm is characteristic of the pyrene excimer. When the polymer concentration increases from 5.8×10^{-3} up to 2 g·dL⁻¹, the locally excited state emission (I_M) is actually observed to increase while the excimer emission (I_E) decreases, in agreement with a transition from intra-

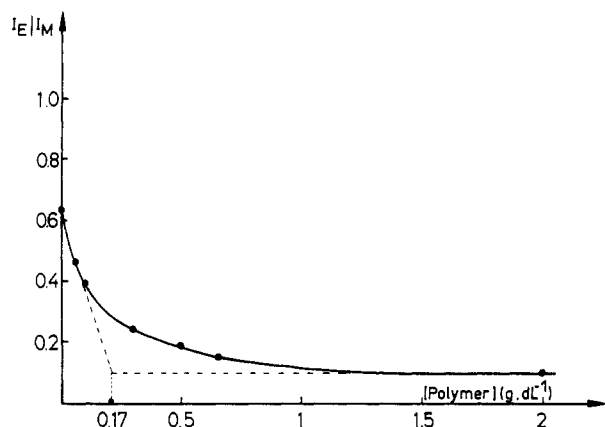


Figure 2. Dependence of I_E/I_M on the concentration of the quaternized α,ω -bis(dimethylamino)polystyrene (\bar{M}_n 12 000) in toluene at 25 °C. I_E and I_M are the intensity emitted by the pyrene excimer and the pyrene locally excited state, respectively. Pyrene concentration is 5×10^{-6} mol·L $^{-1}$.

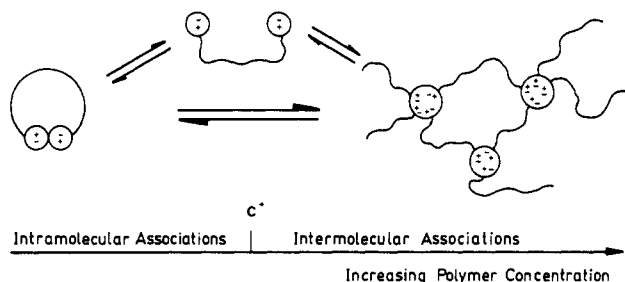


Figure 3. Schematic representation of the association of the ion pairs attached at both ends of polystyrene. Above C^* , the mean number and the average size of multiplets have to change with concentration. (Please read C^* instead of C^* on Figure 3.)

to intermolecular association. This effect is especially pronounced at the lowest polymer concentrations. Figure 2 is a better illustration of the I_E/I_M drop as the polymer concentration increases. Above ca. 1 g·dL $^{-1}$, the intensity emitted by the excimer is very low and nearly constant ($I_E/I_M \sim 0.1$). With the polymer concentration of 6.5×10^{-2} g·dL $^{-1}$ as a reference, the increase in I_E/I_M observed upon decreasing polystyrene concentration down to 5.8×10^{-3} g·dL $^{-1}$ means that the equilibrium conformational state of polystyrene is shifted to the cyclic conformation, i.e., that the intramolecular association of the dipoles attached at both ends of polystyrene has increased (Figure 3). In contrast, when the polymer concentration goes up, the pyrene excimer tends to disappear in favor of the pyrene locally excited state. This means that the intramolecular association of the dipoles is no longer a favorable process and that the equilibrium is displaced toward intermolecular associations (Figure 3). This is in a qualitative agreement with the already mentioned changes in solution viscosity which increase sharply as the polymer concentration increases. Both viscosity and fluorescence results can be rationalized by the intramolecular versus the intermolecular association of the end groups. This mechanism accounts for a chain-extension process and thus for an increase in solution viscosity. Moreover, at the very low pyrene concentration used, the probability for a pyrene-labeled ion pair to be associated to an unlabeled ion pair of another chain has to increase dramatically as the polymer concentration goes up, leading to a drastic restriction of the excimer formation.

The observations reported in Figures 1 and 2 are consistent with a shift from intramolecular to intermolecular associations of the quaternary ammonium end groups of

polystyrene (\bar{M}_n 12 000) dissolved in toluene at 25 °C. The transition should occur approximately at a polymer concentration of 0.17 g·dL $^{-1}$, i.e., the concentration defined by the intersection of the tangents to the portions of the curve (Figure 2) corresponding to the two association modes. As a first approximation, this critical concentration (C^*) should be nothing but the polymer coil overlap concentration (C^*) governed by the electrostatic interactions of the end groups. Of course, this assumption should be supported by the direct determination of the polymer coil overlap concentration (C^*).

Results discussed in this paper emphasize that excimer fluorescence is a very well-suited technique to discriminate intramolecular from intermolecular associations of the ionic end groups of telechelic polymers. By this approach, if C^* actually corresponds to C^* , it might be possible to determine C^* by fluorescence measurements as well as to ensure the effect of parameters, such as polymer molecular weight, solvent polarity, and temperature, on the electrostatic interaction of polymeric ion pairs.

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