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ated with the overall molecular tumbling characterized by the first normal-mode time, τ_1, strongly affected by polydispersity.

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Registry No. $CH_3OC_6H_4C(CH_3)_2C_6H_4OCO_2CH_3$, 124919-83-1; (Bisphenol A)(PC) (SRU), 24936-68-3; (Bisphenol A)(PC) (copolymer), 25037-45-0.

Reaction Rates in Ionomer Solutions. 2. Search for the Kinetic Excluded Volume Effect

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ABSTRACT: The rate of HCl transfer from aminostyrene copolymers of methyl methacrylate to (dimethylamino)ethyl methacrylate copolymers of methyl methacrylate was measured in toluene solution by using a stopped-flow apparatus with fluorescence detection, varying the length of the polymers carrying the interacting groups. Although theories predicted that groups attached close to the polymer chain ends would react faster, no decay of the apparent rate constant with increasing conversion was observed. For reactions between polymers of similar chain length, the rate constant decayed as the 0.6 power of the molecular weight. When the interacting groups were attached to polymers which are immiscible in bulk, the HCl transfer rate was reduced. Solvation of the aminostyrene hydrochloride residues by methanol or ethyl acetate accelerated sharply the reaction rate. There was no evidence for an effect on the reaction rate when sufficient poly(methyl methacrylate) was added to the solution of the interacting copolymers to exceed the critical chain overlap concentration.

Introduction

Recently, we embarked on a study of the kinetics of reactions involving the ion pairs in ionomer solutions. In the first investigation of this type,[1] we mixed in a stopped-flow apparatus solutions of slightly sulfonated polystyrene partially neutralized with 2-(aminomethyl)naphthalene and 9-(aminomethyl)anthracene, respectively. As long as these counterions were associated with different polymer chains, irradiation in the naphthalene absorption band led to little nonradiative energy transfer,[2] since the donor and acceptor fluorophores were too distant from one another. However, increasing counterion interchange led to an increasing association of both counterions with the same chain molecule, and the increasing efficiency of energy transfer (i.e., emission from the

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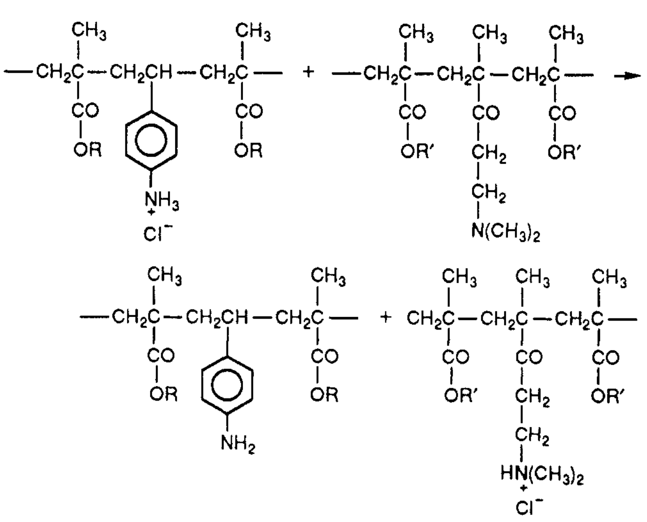
anthracene moiety on irradiation of the naphthalene chromophore) could be used to monitor the counterion interchange process. It should be noted that such a study is of general physicochemical interest, since the use of ionomers may be regarded merely as a convenient device to keep ion pairs dissolved in nonpolar media.

In the present study, we investigated the rate at which HCl is transferred from an alkyl methacrylate copolymer containing a small fraction of *p*-aminostyrene residues to alkyl methacrylate copolymers containing the more basic aliphatic amine groups:



Since the fluorescence of the aminostyrene residues is quenched by protonation, the HCl transfer may be followed by the increasing fluorescence intensity. Our main interest in this study concerned the extent to which the length and the nature of the polymer chains to which the interacting functional groups were attached affected the reaction rate constant.

In considering reactions between groups attached to different polymer chains, we have to distinguish between diffusion-controlled processes and reactions involving substantial activation energies.

An important example of a diffusion-controlled polymer reaction is the macroradical recombination in free radical polymerization, and the chain length dependence of this process was first studied by North and his collaborators.[3] They concluded that it is not the diffusion of the polymer chains toward each other but rather the micro-Brownian diffusion of the free radical chain ends toward the surface of the molecular coils, where they are accessible to mutual interaction, which is rate limiting. As discussed by Horie et al.[4] and by Mahabadi and O'Driscoll,[5] the rate of this segmental diffusion depends on the solvent viscosity, the chain length of the polymers, the excluded volume effect, and the chain flexibility. Another approach to the study of diffusion-controlled interpolymer reactions utilized the quenching of the phosphorescence of benzil residues at the end of polystyrene chains by anthracene-terminated polystyrene.[6] The quenching rate constant k_q was found to decrease as the 0.29 power of the chain length. If the effect of the solvent viscosity η_0, and the temperature T is taken into account, the "reduced rate constant" $k_q\eta_0/T$ was found to be larger in good solvents for polymerization degrees below 1000 while the opposite trend held for longer polymer chains. Mita et al.[7] studied the interaction of these end-labeled polystyrenes in the presence of the unlabeled polymer and found that below the critical overlap concentration C^* (ref 8) k_q increased with an increasing concentration of polystyrene in benzene but decreased in cyclohexane solution. These trends paralleled the concentration dependence of the diffusion coefficient measured under a macroscopic concentration gradient in these two media. In benzene solution containing 50–100 g/L of polystyrene, k_q was found to be independent of the length of the end-labeled polymers. A general review of studies of diffusion-controlled interpolymer reactions was presented by Mita and Horie.[9]

In considering interpolymer reactions with substantial activation energies, Flory's studies of the kinetics of polycondensations,[10] in which he demonstrated that the reaction rate constants characterizing two interacting groups are independent of the length of chains to which they are attached, may serve as a suitable point of departure. Yet, in discussing this principle in his classical monograph, Flory[11] conceded the possibility that "the terminal group of a very large polymer molecule will be shielded by the coiling of the chain and its reaction rate will be reduced...in very dilute solutions where sufficient space is available to permit the polymer molecules to exist more or less independently of one another". Flory never returned to this argument, and it has, to our knowledge, been generally overlooked and never been quoted. Because the expected decrease of the reaction rate constant under these conditions is due to the entropic resistence of flexible chains to interpenetration, which also accounts for the large excluded volume revealed in the osmotic behavior, we have referred to it as the "kinetic excluded volume effect".[12]

Several approaches have been used to estimate the magnitude of the effect. In one approach,[12–14] the ratio of the rate constant k characterizing polymer-bound reactive groups and k_0, the corresponding rate constant of their low molecular weight analogues, is calculated from the contributions of all degrees of interpenetration of the macromolecular coils taking account of the excluded volume effect. More recently, Olaj and Zifferer[15] have studied k/k_0 by a Monte-Carlo simulation for athermal and Θ solutions. It may be noted that in these approaches no account was taken of the possible effect of conformational mobility of the polymer coils on k/k_0. Alternatively,[12,16,17] k/k_0 was assumed to be given by Q_{AB}^*/Q_AQ_B, where Q_{AB}^* is the conformational partition function of the transition-state complex in which the two polymers are linked and Q_A and Q_B are the conformational partition functions of the two separate chains.

The experimental evidence is contradictory. All theoretical treatments predict that k/k_0 should depend on the location along the polymer chain at which the reactive groups are attached, with the "kinetic excluded volume effect" least pronounced for the interaction of end-labeled polymers. Data for the rate of coupling of end-labeled polymers in highly dilute solutions are available from two laboratories. Black and Worsfold[18] found a substantial decrease in the second-order rate constant when the concentration of the interacting polymers was reduced below the critical overlap concentration. By contrast, Okamoto et al., who studied two different polymer coupling reactions,[19,20] found no change in the reaction rate constant over a molecular weight range from 20 to 20 000. Black and Worsfold also studied coupling reactions between polymers carrying a single reactive group attached at random along the chain backbone and found, as expected, that such reactions are slower than those between polymers substituted at their chain ends. When comparing interpolymer reactions with complex formation between two polymers carrying a single acid and base group, respectively, Worsfold[21] found that the apparent resistance due to the interpenetration of the polymer chains is more pronounced if the interaction of the polymer-bound groups has to lead to a covalent bond formation.

Evidence for a "kinetic excluded volume effect" has been reported by Wetmur and Davidson[13] in their study of the "renaturation" of DNA, in which two separated strands of the nucleic acid reconstitute the native double-helical structure. However, this process involves the interaction of two chains with a high density of electrical charge, so that the effect would be expected to be much larger than in reactions of uncharged polymers.

The sensitivity of spectroscopic techniques imposes a limit on the length of polymer chains containing a single reactive group whose reaction can be followed in solutions below the critical overlap concentration. On the other hand, if each of the interacting chains carries more than a single reactive group, the first bond joining these chains will bring the other interacting groups close to one another, increasing the rates of subsequent reactions.[16] To avoid such complications, we have studied in the past[22,23] reaction kinetics in solutions containing chain molecules carrying reactive groups and chain molecules to which residues acting as catalysts for reactions of these groups were attached. The results of these studies deviated in several respects from the expected pattern. They followed first-order kinetics, although the expected dependence of the rate constant on the distance of the point of attachment of the reactive and catalytic groups from the polymer chain end should have led to a dispersion of the rate constant. The reaction rates exhibited little dependence on the chain length, and k/k_0 was smaller in a poorer solvent medium. Attachment of the interacting groups to different polymers, immiscible with each other, which would have been expected to enhance the excluded volume effect, did not lead to a decrease of k/k_0.

In these studies, we used UV spectroscopy to monitor the reaction, and with this analytical tool we were not able to study reaction rates as far below the critical overlap concentration of the polymers as we would have wished.[23] Since fluorescence provides a much more sensitive analysis, we were able to improve on this feature in the present investigation.

Experimental Section

Materials. Ethyl acetate was refluxed with acetic anhydride in the presence of several drops of concentrated sulfuric acid and fractionally distilled. The distillate was shaken with anhydrous potassium carbonate, filtered, and redistilled. Anhydrous toluene and spectroscopic grade methanol were used without further purification. All monomers were distilled under vacuum before use. Copolymers of alkyl methacrylates with *p*-aminostyrene (AS) (Polysciences) or (*N*,*N*-dimethylamino)ethyl methacrylate (DMAEMA) (Polysciences) were prepared either in dioxane solution or in bulk at 60 °C by using AIBN initiator. *N*-dodecyl mercaptan (1–3%) was added to the polymerization mixture to prepare copolymers with molecular weights below 50 000. Conversions were kept below 20% so as to minimize a drift in the composition of the copolymers. All polymers were purified by three precipitations from dioxane solution into methanol or hexane and vacuum-dried at room temperature for several days. The aminostyrene content in the copolymers was determined from the absorption in dioxane solution at 291 nm by using the extinction coefficient of 2090 cm^{-1} M^{-1} for toluidine.[24] The DMAEMA content was determined by titration in methanol–benzene (20/80) solution with 0.01 N HCl in the same solvent mixture and methyl orange as the end point indicator. The molecular weight of methyl methacrylate copolymers was either estimated from the intrinsic viscosity in chloroform at 25 °C (using the Mark–Houwink constants for poly(methyl methacrylate)[25]) or determined by GPC. The GPC trace showed no significant change in the copolymer polydispersity for the samples prepared in the presence of the chain transfer agent. Table I lists the designations, compositions, intrinsic viscosities, and molecular weights of the copolymers used in this study.

Table I
Characterization of Polymers

polymer	mol % AS	mol % DMAEMA	$[\eta]$, dL/g	$\bar{M}_w$ or $\bar{M}_n$
PMMA–AS-a	0.73		1.09	280 000[a]
PMMA–AS-b	1.46		0.83	196 000[a]
PMMA–AS-c	1.00		0.24	41 000[b]
PMMA–AS-d	1.16			21 000[b]
PMMA–DMA-a		0.98	0.95	234 000[a]
PMMA–DMA-b		2.32	1.10	280 000[a]
PMMA–DMA-c		1.79	1.22	320 000[a]
PMMA–DMA-d		1.79	0.69	150 000[a]
PMMA–DMA-e		1.62	0.29	53 000[b]
PMMA–DMA-f		1.57		23 600[b]
PEMA–DMA		2.00	0.92	
PBMA–DMA		2.19	0.92	
PBMA–AS	0.74		0.90	

[a] From GPC data. The $\bar{M}_w/\bar{M}_n$ ratio was less than 1.8. [b] From intrinsic viscosities in chloroform at 25 °C.

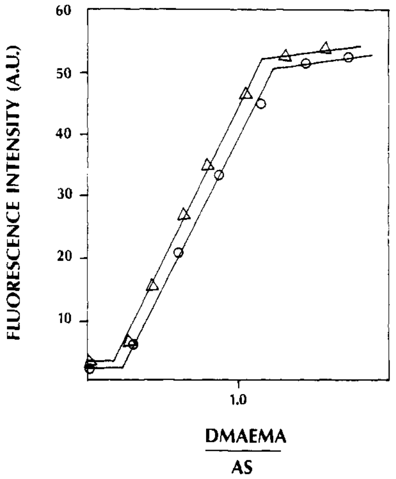


Figure 1. Fluorescence titration of PMMA–AS hydrochloride with PMMA–DMA: (△) PMMA–AS-c hydrochloride titrated with pMMA–DMA-e; (○) PMMA–AS-b hydrochloride titrated with PMMA–DMA-b.

Solution Preparation. Since the hydrochloride of the aminostyrene copolymers could not be dissolved in toluene, solutions of these ionomers were prepared by passing HCl gas (dried by passage through concentrated sulfuric acid) through the AS copolymer solution. The excess HCl was removed by alternating a stream of nitrogen and a vacuum. The nitrogen was dried by passage through powdered potassium hydroxide and powdered phosphorus pentoxide. Any excess of HCl remaining was determined by a titration of the protonated AS copolymer with a toluene solution of a DMAEMA copolymer following the emission intensity at 338 nm, the emission maximum characteristic of the basic form of the AS residues. Since we may assume that the transfer of the HCl from the aromatic amine to the aliphatic amine is quantitative, the location of the break in the titration curve indicates the concentration of the excess HCl in the protonated AS copolymer solution. A Perkin-Elmer MPF-44B fluorescence spectrophotometer was used in these titrations. Figure 1 shows two typical titration curves.

All ionomer solutions were prepared shortly before use. Concentrations of copolymers were specified in terms of the molarity of the AS and DMAEMA monomer residues.

Kinetics. Solutions of the protonated AS copolymer and the DMAEMA copolymer containing an equal concentration of interacting groups (with the DMAEMA residue concentration reduced by the concentration of free HCl in the AS copolymer

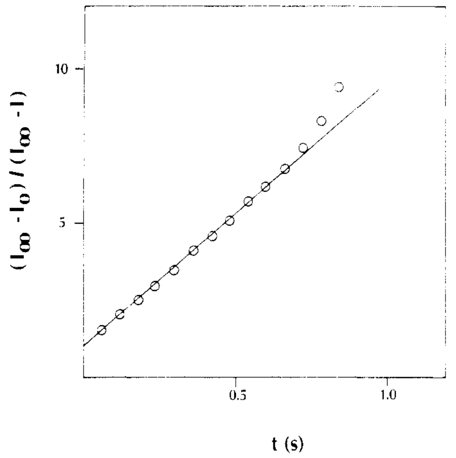


Figure 2. Second-order plot of the HCl transfer from PMMA-AS-b to PMMA-DMA-b ($c_0 = 1.1 \times 10^{-4}$ M).

Table II
Rate Constant of HCl Transfer from PMMA-AS-b to PMMA-DMA-c as a Function of the Initial Reagent Concentration[a]

10^4c_0, M	$10^{-4}k_2$, M^{-1} s^{-1}
0.37	8.7
0.74	7.0
1.10	7.5
1.47	8.0
1.84	9.3

[a] Toluene solution at 7 °C.

solution) were mixed in the stopped-flow apparatus with fluorescence detection described previously.[26] The solution was irradiated at 300 nm, where the absorption by toluene is negligible. A Corning Glass filter CSG-45 with a cutoff at 310 nm was used to isolate the aminostyrene residue emission from the excitation light. Each kinetic run was repeated at least 10 times, with the data averaged by a dedicated computer. Unless stated otherwise, all runs were carried out at 7 °C in toluene solution.

Results and Discussion

Nature of the Kinetics. After the mixing of the AS copolymer hydrochloride and DMAEMA copolymer solutions in the stopped-flow apparatus, the first meaningful reading of the emission intensity, I_0, corresponded to a reaction time t = 1 ms. Such readings were identical with those obtained when the solution of the protonated AS copolymer was diluted with an equal volume of toluene, indicating that we were able to follow the whole of the HCl-transfer reaction. This was not so in the reaction of the protonated AS copolymers with the DMAEMA *monomer*, for which the reaction is too fast, so that we could follow only about the last 40% of the process. The reaction of the two copolymers exhibited the following features:

(1) Within experimental error, the time dependence of the emission intensity of the AS residues, $I(t)$, followed in all cases an approach to its equilibrium value I_∞ given by

$$\frac{I(t) - I_0}{I_\infty - I(t)} = c_0k_2t \tag{1}$$

where c_0 is the initial reagent concentration and k_2 the second-order rate constant. This is illustrated in Figure 2, where a plot according to relation 1 is seen to be linear up to a conversion > 50%. The k_2 value was also found to be independent of the initial reagent concentration, as illustrated in Table II and Figure 3, where the time required for the emission intensity to move halfway from I_0 to I_∞, $t_{1/2}$, is shown to be inversely proportional to c_0. The strict conformity of the reaction to second-order kinetics and the constancy of the second-order rate constant over a wide range of concentration of the reactive polymers carry some important implications: (a) Intramolecular associations of the ion pairs in the protonated AS copolymer are probably quite small at the low (~1 mol %) concentration of AS residues in the copolymer; in addition, ion-pair association may not lead to any marked change in the rate of the proton-transfer reaction. (b) Since all experiments were carried out well below the critical polymer overlap concentration, intermolecular ion-pair association was not expected to be important[31] (though possibly present to a very slight extent[32]), so the unchanged value of the rate constant in this range of ionomer concentrations is not surprising. (c) There is no evidence for a dependence of the reactivity of the interacting groups on the distance of their attachment from the ends of the polymer chain, as predicted by theoretical analysis[16,17] and by computer simulation,[12,15] since this would lead to a dispersion of the rate constant. This conclusion, based on the present results, agrees with previous findings in this laboratory[22,23] but contrasts with the results of Black and Worsfold,[18] who observed faster reactions for groups attached to the ends of polymer chains than for groups distributed at random along the length of the chain molecules. (d) As the proton transfer proceeds, the ion-pair density decreases in the AS copolymer and increases in the DMAEMA copolymer. This should result in an expansion of the first and a contraction of the second species. Also, the mixing of the two copolymers, each carrying amine hydrochloride groups,[36] should be more favorable than that of the AS hydrochloride copolymer with the uncharged copolymer of DMAEMA. The constancy of the rate constant up to 50% conversion suggests that these factors do not influence the kinetics of the proton transfer significantly.

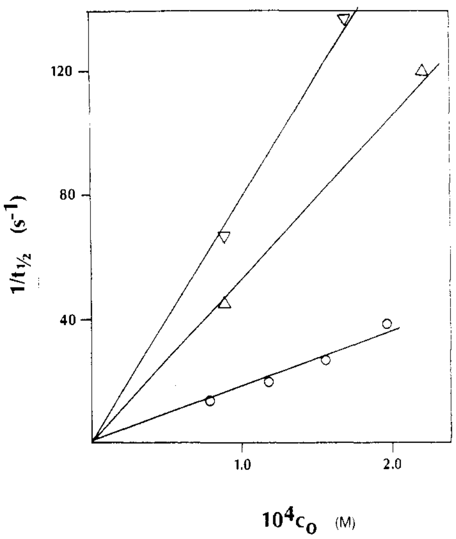


Figure 3. Dependence of $1/t^{1/2}$ on the initial concentration c_0 of interacting groups: (▽ PMMA-AS-d (M = 21 000) reacting with PMMA-DMA-f (M = 23 600); (△) PMMA-AS-c (M = 41 000) reacting with PMMA-DMA-e (M = 53 000); (○) PMMA-AS-a (M = 280 000) reacting with PMMA-DMA-b (M = 280 000).

(2) The temperature dependence of the HCl-transfer reaction was determined by using copolymers PMMA-AS-a and PMMA-DMA-c with an initial concentration of reactive groups $c_0 = 9.8 \times 10^{-5}$ M. The rate constants of 13.9×10^4, 20.4×10^4, and 30.6×10^4 at 7, 12, and 17.5 °C, respectively, corresponded to $\Delta H^* = 11.7$ kcal/

Table III
Dependence of HCl-Transfer Rate Constant on Polymer Chain Length[a]

molecular weight		
PMMA-AS	PMMA-DMA	$10^{-4}k_2$, M^{-1} s^{-1}
21 000	23 600	79.5 ± 2.3
	53 000	70.1 ± 4.2
	150 000	67.5 ± 2.4
	320 000	62.3 ± 1.8
41 000	53 000	52.4 ± 2.0
	150 000	37.8 ± 0.9
	320 000	38.1 ± 1.8
280 000	53 000	32
	150 000	17
	280 000	17.5 ± 1.6
	320 000	14

[a] Toluene solution at 7 °C. The margins of error in the k_2 values represent one standard deviation.

mol and $\Delta S^{*} = 6$ eu. The reaction was, therefore, not diffusion controlled.

In the following discussion, k_2 for the HCl transfer was obtained either by fitting the kinetic data by eq 1 or from $k_2 = 1/c_0t_{1/2}$.

Rate of HCl Transfer as a Function of the Polymer Chain Length. In trying to assess the "kinetic excluded volume effect", we should compare the reaction rate of functional groups attached to two polymer chains to the reaction rate of similar groups carried by compounds of low molecular weight. In our case, this is not possible since *p*-toluidine, which may be considered a low molecular weight analogue of the AS residues in AS copolymers, becomes insoluble in toluene solution when it is converted to its hydrochloride. When PMMA-AS-a hydrochloride was mixed with the DMAEMA *monomer*, the part of the HCl-transfer process which we were able to follow in our stopped-flow apparatus corresponded to a rate constant of 560 × 10^4 M^{-1} s^{-1}.

In a reaction involving a reagent of low molecular weight with a functional group attached to a polymer, the rate constant may differ from that of two analogous low molecular weight reagents for two reasons:[27,14] (a) The small reagent behaves like a cosolvent, and its relative affinity for the polymer may lead to either its concentration in the polymer domain or its exclusion from it. (b) If the reaction is sensitive to the nature of the solvent medium, a difference between this medium in the immediate vicinity of the polymer and the bulk of the solvent will lead to a change in the reaction rate. On the other hand, in reactions in which both interacting groups are attached to similar polymer chains, changes in local concentration due to solvation effects would not be expected, and the effective local reaction medium will be different from that of a reaction of a group attached to a polymer with a low molecular weight reagent. Thus, the reactions of a methyl methacrylate copolymer carrying AS hydrochloride residues with a DMAEMA monomer and its methyl methacrylate copolymers are not strictly comparable. Still, it is striking that k_2 for the reaction of PMMA-AS-a hydrochloride with the DMAEMA monomer is larger by 1 order of magnitude as compared to the rate constants for the analogous interpolymer reactions of various PMMA-AS hydrochlorides with various PMMA-DMA species (Table III and Figure 4).

The rate constants for the interpolymer reactions decreased significantly with an increasing length of the polymer chains to which the interacting groups were attached. When the molecular weight of the PMMA-AS hydrochloride was kept constant, k_2 decreased with an increasing chain length of the PMMA-DMA and appeared to level off for very high molecular weights of the second polymeric reagent. The relative change of k_2 was small for short PMMA-AS chains but became much more pronounced for larger PMMA-AS species. When the two interacting copolymers had similar chain lengths, k_2 decreased about fivefold as the molecular weights increased from ~20 000 to 280 000. When the two copolymers had different molecular weights, it did not appear to matter which reagent was attached to the longer chain: for the reaction of PMMA-AS-c (MW 41 000) with PMMA-DMA-c (MW 320 000) and the reaction of PMMA-AS-a (MW 280 000) with PMMA-DMA-e (MW 53 000), the rate constants were similar, 38 and 32 M^{-1} s^{-1}, respectively.

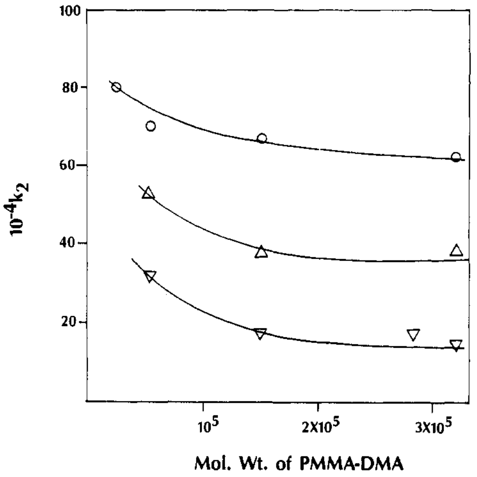


Figure 4. Dependence of the rate of HCl transfer from PMMA-AS to PMMA-DMA on the molecular weights of the interacting polymers: (○) PMMA-AS-d (M = 21 000); (△) PMMA-AS-c (M = 41 000); (▽) PMMA-AS-a (M = 280 000).

Rate of HCl Transfer between Groups Attached to Chemically Different Chain Molecules. So far, we have considered reactions between groups attached to similar polymer chains, so that the "kinetic excluded effect" would have been due to the entropic resistence of flexible chain molecules to chain overlap. When the chains carrying the reactive groups are different, the energetic interaction between them would be expected to have an additional effect on the interpolymer reaction rate.[22] In the absence of specific interactions, the mixing of different polymers is generally endothermic, rendering such polymers immiscible, and this has been shown specifically to be the case for mixtures of PMMA with poly(ethyl methacrylate) (PEMA) and poly(butyl methacrylate) (PBMA).[28] Even in dilute solution, where there is no phase separation, the energetically unfavorable mixing should impede chain overlap and thus reduce interchain reaction rates. This expectation was confirmed when we compared the HCl-transfer rates between a protonated PMMA-AS copolymer with PMMA-DMA, PEMA-DMA, and PBMA-DMA copolymers (Figure 5).

We were surprised to find that when the protonated AS was attached to a butyl methacrylate copolymer the rate of HCl transfer was the same, within experimental error, for the reactions with PBMA-DMA and PMMA-DMA (Table IV). However, Frank and Gashgari[29] estimated solubility parameters δ for PMMA, PBMA, and polystyrene as 9.25, 8.60, and 9.04, respectively. Since Burell[35] lists δ for benzene and aniline as 9.2 and 10.3, we may assume that δ for a styrene residue is increased by amine substitution so as to be larger than that of a methyl methacrylate residue. Since δ should be similar

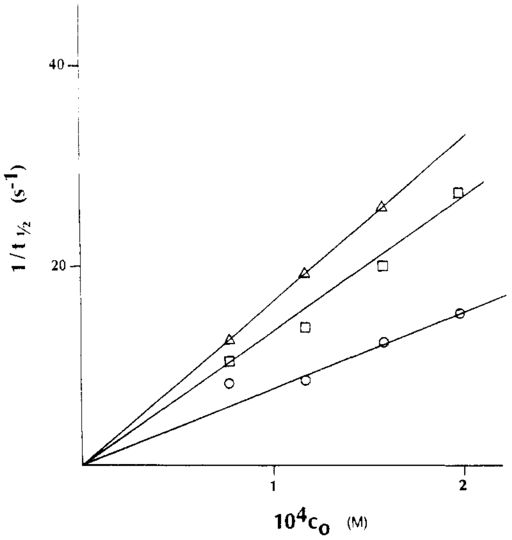


Figure 5. Transfer of HCl from PMMA-AS-a to PMMA-DMA-b (△), PEMA-DMA (□), and PBMA-DMA (○).

Table IV
Rate Constants for HCl Transfer from PBMA-AS to PMMA-DMA-b and PBMA-DMA[a]

	$10^{-4}k_2$, M^{-1} s^{-1}	
10^4c_0	PBMA-DMA	PMMA-DMA-b
0.393	22	
0.785	20	
0.840		18
1.18	17	
1.57	17	
1.66		21
1.96	19	

[a] Toluene solution at 7 °C.

for a butyl methacrylate and a DMAEMA residue, we conclude that the difference between δ of PMMA and PBMA is increased when AS residues are attached to PMMA but reduced if they are attached to PBMA chains. In fact, we found that a film cast from a toluene solution of equal weights of PBMA-AS and PMMA-DMA-b was almost transparent, while a film containing PMMA-AS-a and PBMA-DMA separated into two phases.

Dependence of PMMA-AS Reactivity on the Concentration of AS Residues in the Copolymer. In nonpolar media, ionomer behavior is dominated by the strong tendency of polymer-bound ionic groups and their counterions to form ion pairs which associate with each other.[30,31] Although viscosimetry has been interpreted as indicating that in dilute solution the ion-pair association is intramolecular,[31a] more recent neutron-scattering studies[32] have shown that intermolecular ionomer association is significant well below the critical chain overlap concentration. Since both intramolecular and intermolecular association of the ion pairs should increase with an increasing density of these ion pairs along the polymer chain backbone, the reactivity of the AS hydrochloride residues might change as their content in the copolymer is varied.

We studied this factor by comparing the reaction rate of PMMA-DMA-b with PMMA-AS-a and PMMA-AS-b, which contained AS residue concentrations of 0.733 and 1.46 mol %, respectively. As seen in Figure 6, the increase in the AS hydrochloride concentration leads to a 50% reduction of the reaction rate. We were unable to extend this study to PMMA-AS copolymers with higher AS concentrations. When the AS content was 2.6 mol %, the copolymer precipitated from toluene solution as it was converted to its hydrochloride. Since an increase in the density of AS hydrochloride residues brings the ionomer close to the precipitation point, the polymer chain must contract, and this may be the cause of the decreased reaction rate with the PMMA-DMA copolymer.

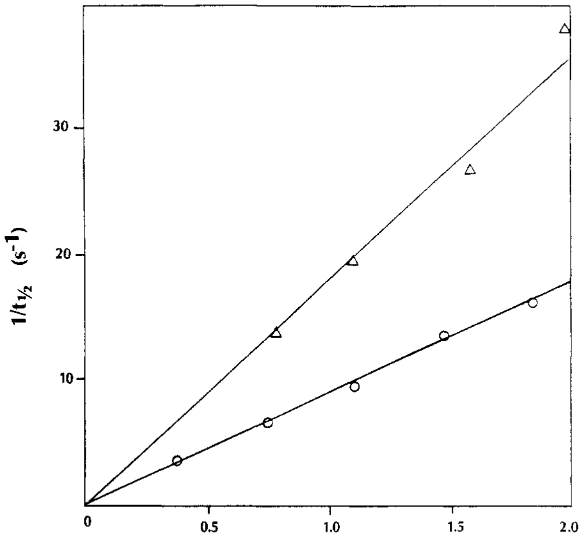


Figure 6. Transfer of HCl from PMMA-AS-a (0.73 mol % AS residues) (△) and from PMMA-AS-b (1.46 mol % AS residues) (○) to PMMA-DMA-b.

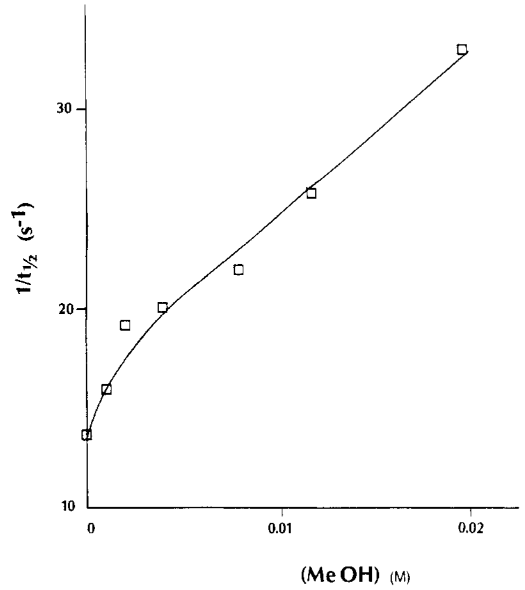


Figure 7. Effect of methanol cosolvent on the transfer of HCl from PMMA-AS-a to PMMA-DMA-c.

Effect of Ion-Pair Solvation on the Rate of the HCl Transfer. Lundberg and Makowski[33] found that the addition of small amounts of a cosolvent such as hexanol to a hydrocarbon solution of an ionomer leads to a large reduction of the solution viscosity. This was interpreted as due to a destabilization of the ion pairs as they became more highly solvated. It would then be expected that addition of small concentrations of an alcohol to a toluene solution of PMMA-AS hydrochloride would accelerate the HCl transfer to PMMA-DMA. Our experiments fully confirmed this expectation. As shown in Figure 7, the HCl-transfer rate was more than doubled when 0.02 M methanol was added to the toluene solution of the two interacting polymers.

The sensitivity of the reaction rate to small concentrations of methanol raised the question whether small amounts of water in the "anhydrous" toluene used as the solvent in our experiments might not also have affected the results. To check on this point, toluene was subjected to a rigorous drying procedure by refluxing and distilling over sodium. No change was observed in the reaction rate of PMMA–AS hydrochloride with PMMA–DMA when using as a solvent toluene subjected to this procedure.

Effect of PMMA Addition on the Rate of HCl Transfer from PMMA–AS Hydrochloride to PMMA–DMA. All the experiments described so far were carried out at a polymer dilution more than 1 order of magnitude below the critical chain overlap concentration. In solutions containing higher concentrations of the reactive copolymers, the reaction would have been too fast to be followed in our stopped-flow apparatus. To determine how higher polymer concentrations influence the reaction kinetics, we added, therefore, methyl methacrylate homopolymer to the solution containing the reactive copolymers PMMA–AS hydrochloride and PMMA–DMA-b. The reaction rate was found to be linear in the PMMA concentration, with k_2 increasing from 17 to 38 $\times 10^4$ M^{-1} s^{-1} when 3.3 g/dL of PMMA was added. However, since the addition of 1 vol % of ethyl acetate to the toluene solution of the interacting polymers led also to an increase of the rate constant to 36 $\times 10^4$ M^{-1} s^{-1}, it appears that this acceleration of the reaction reflected an increased solvation of the ion pairs rather than the increased polymer concentration. Since the PMMA used in this experiment had an intrinsic viscosity of 0.68 dL/g in toluene solution, a concentration of 3.3 g/dL corresponded to $c[\eta] = 2.2$, i.e., to conditions where polymer chain entanglements should be significant.[34] This was not reflected in the interpolymer reaction rate.

Concluding Remarks

The results of the present study provide clear evidence for a "kinetic excluded volume effect". The rate constant observed in the reaction of the PMMA–AS hydrochloride with the DMAEMA monomer was 7 times as high as the rate constant for the HCl transfer between two polymers with molecular weigths ~20 000. Although the DMAEMA may be a somewhat better solvent than toluene for PMA–AS, leading to its increased concentration in the polymer domain, this effect would be expected to be minor. It can certainly not account for the large difference between the rate constants characterizing the polymer-bound AS hydrochloride interaction with the aliphatic amine monomer and a similar group attached to a polymer chain.

The observation that the interpolymer reaction followed strictly second-order kinetics up to a conversion of about 50% is inconsistent with the prediction of all theories that interpolymer reaction rate constants should increase as the point of attachment of the interacting groups approaches the polymer chain ends. We may note that the expected dispersion of the rate constant was not observed in two previous studies in this laboratory involving interpolymer reactions between groups attached at random along the length of polymer chains.[22,23] We have no explanation for this feature of the results.

When reaction rates between groups attached to polymers of similar length are compared, the rate constant is found to be proportional to the 0.6 power of the molecular weight. This is the dependence predicted by Kholkhov[17] for the interaction of groups attached to the center of polymer chains. However, since even a small number of ion pairs carried by a polymer lead to a pronounced chain contraction, the mixing of PMMA–AS hydrochloride with PMMA–DMA may not be athermal as assumed in the theoretical treatments. We have observed a tendency for the apparent second-order rate constant to increase for conversions exceeding 50%, and this might be attributed to the fact that at this stage both polymers carry comparable concentrations of ion pairs favoring their interpenetration.

As the polymer concentration is increased beyond the critical overlap concentration c^*, the effect of the shielding of the reactive groups in the interior of the polymer coils should disappear. Yet, we found in the present work and in a previous study[23] no evidence for such behavior. Unfortunately, the high viscosity of solutions beyond c^* sets a limit to the concentration range which can be studied in the stopped-flow apparatus.

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Thermodynamic Predictions of Volume Changes in Temperature-Sensitive Gels. 1. Theory

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ABSTRACT: This paper presents a molecular theory of swollen gels based on a compressible lattice model. The theory extends the Sanchez and Lacombe lattice-fluid model for polymer solutions through addition of the elastic term of the Flory–Rehner theory of rubber swelling. The characterization of this type of binary mixture requires knowledge of pure component parameters and an interaction energy correction characteristic of each binary mixture. The four basic types of liquid–gel phase diagrams predicted are related to the presence of upper and lower consolute temperatures or closed immiscibility loops in solution of the uncross-linked polymer.

Introduction

Temperature-sensitive gels can be used to concentrate dilute solutions or to alter drug release. For example, such gels have been used to produce soy protein isolate[1,2] and to alter insulin release.[3-5] As such, they are a new technology of practical significance.

These gels swell when they are placed in water. The swelling occurs because the polymer is hydrophilic; it is constrained because of chemical cross-links present between the polymer chains. However, the swelling varies sharply with temperature. For example, poly(isopropylacrylamide) gel swells to 30 times its dry volume in water at 34 °C but only 4 times its dry volume at 35 °C.[1,6]

Such violent changes in swelling occur because of the proximity of a consolute point in the homologous uncross-linked polymer. They can be induced by changes in pH,[7] by the application of electrical fields,[8] by the addition of mixed solvents,[9] or by pressure.[10]

A theory of these swelling transitions must include both the solution characteristics of the uncross-linked polymer chains and the elastic effects introduced by the cross-links. The experimental phase diagram of Figure 1 illustrates both features. The uncross-linked polymer is shown as squares, and the cross-linked gel is shown as triangles. The region above the squares is a two-phase region, consisting of a water-rich phase and a polymer-rich phase. Below 31 °C, the polymer and water are completely miscible; above this temperature they become only partially miscible. The minimum on this curve is a "lower consolute point" or "lower critical solution temperature" (LCST).

The phase behavior of the gel above 34 °C is like that of the uncross-linked polymer, forming pure water and a polymer-rich phase. The pure water phase contains no gel because the presence of cross-links does not allow the complete dissolution of the gel. The gel below 34 °C may exist as a homogeneous gel phase or as a highly swollen gel in equilibrium with excess water.[2,11]

The behavior in Figure 1 is part of the general behavior of uncross-linked polymers shown in Figure 2.[12-14] Of the three two-phase regions A, B, and C shown there, only the lower portion of C, including the critical point labeled LCSTII, is covered by the temperature range of Figure 1. Region A is the normal-phase separation predicted by the original Flory–Huggins model. Here polymer–solvent miscibility is governed by the energy of forming contacts between polymer segments and solvent at essentially constant volume, even under constant pressure conditions. The dominant consideration in region B is that the solvent is approaching the critical point of its liquid–vapor curve; mixing at constant pressure here produces large changes in the total volume. In region C, miscibility is determined by a complex interplay between polymer–solvent interactions and volume changes. Part of the complexity arises from the fact that the thermodynamic functions both of the mixture and of the pure components are affected in nontrivial ways by thermal expansion.

These considerations have been developed along rather different lines into quantitative theories by Flory[14] and by Sanchez and Lacombe.[15] In this paper we combine the more tractable model of Sanchez and Lacombe with Flory's treatment of network swelling to obtain a theory of swelling transitions. Comparison with experiment will be the subject of a second paper.

Theory

The starting points for the model of this gel are the Sanchez and Lacombe theory of mixing and the Flory–Rehner theory of rubber elasticity.[14-16] The gel's partition function is as a first approximation separated into elastic and mixing factors,[17-19] and the Helmholtz free

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