However, for at least the heavier paraffins,[7,8] 1,3-DMA (present work), and 5α-cholestane[6] in rubbers, the internal friction between these molecules is apparently high enough to replace the effects of the constraining polymer chains without noticeable transition. Because the mass of all diluent molecules is the same, this internal friction cannot originate in differential inertial confinement.[22] We tentatively suggest that larger diluent molecules may not find the polymer molecular segments to be effective constraints; collisions between large diluent molecules and segments may displace these segments as effectively as they would other diluent molecules. In that case no diffusivity enhancement at high diluent content is observed because the enhancement exists at all concentrations.

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References and Notes

(1) See for example: Hertz, H. G. *Ber. Bunsenges. Phys. Chem.* **1971**, *75*, 183.
(2) A comprehensive review appears in: "Diffusion in Polymers"; Crank, J., Park, G., Eds.; Academic Press: New York, 1968; Chapters 2, 3, 4, and 8.
(3) Kessler, D.; Witte, H.; Weiss, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 368.
(4) Vrentas, J. S.; Duda, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 403.
(5) Vrentas, J. S.; Duda, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1085.
(6) von Meerwall, E.; Ferguson, R. D. *J. Chem. Phys.* **1981**, *75*, 937.
(7) von Meerwall, E.; Ferguson, R. D. *J. Appl. Polym. Sci.* **1979**, *23*, 3657.
(8) Ferguson, R. D.; von Meerwall, E. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1285.
(9) Stejskal, E. O.; Tanner, J. E. *J. Chem. Phys.* **1965**, *42*, 288.
(10) Van Antwerp, R.; von Meerwall, E. *Bull. Am. Phys. Soc.* **1982**, *27*, 627.
(11) Bueche, F. "Physical Properties of Polymers"; Interscience: New York, 1962; Chapter 5.
(12) Fujita, H. *Fortschr. Hochpolym.-Forsch.* **1961**, *3*, 1.
(13) Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955**, *77*, 3701.
(14) The physical and chemical data were supplied by Sun Oil Co.
(15) von Meerwall, E.; Ferguson, R. D. *J. Appl. Polym. Sci.* **1979**, *23*, 877.
(16) von Meerwall, E.; Burgan, R. D.; Ferguson, R. D. *J. Magn. Reson.* **1979**, *34*, 339.
(17) von Meerwall, E. *Comput. Phys. Commun.* **1979**, *17*, 309.
(18) von Meerwall, E. *Comput. Phys. Commun.* **1979**, *18*, 411.
(19) Ferry, J. D. "Viscoelastic Properties of Polymers", 3rd ed.; Wiley: New York, 1981; p 277.
(20) Carman, P. C.; Stein, L. H. *Trans. Faraday Soc.* **1956**, *52*, 619.
(21) Frenkel, J. "Kinetic Theory of Liquids"; Dover: New York, 1955.
(22) von Meerwall, E.; Ferguson, R. D. *J. Chem. Phys.* **1980**, *72*, 2861.
(23) Rhee, C.-K.; Ferry, J. D.; Fetters, L. J. *J. Appl. Polym. Sci.* **1977**, *21*, 783.
(24) Cohen, M. H.; Turnbull, D. *J. Chem. Phys.* **1959**, *31*, 1164. Turnbull, D.; Cohen, M. H. *Ibid.* **1961**, *34*, 120.
(25) Boss, B. D.; Stejskal, E. O.; Ferry, J. D. *J. Phys. Chem.* **1967**, *71*, 1501.

Controlled Release of Fluoride Ions from Methacryloyl Fluoride–Methyl Methacrylate Copolymers. 2. Solution Hydrolysis and Release of Fluoride Ions

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ABSTRACT: The hydrolysis of acid fluoride groups in methacryloyl fluoride (MF)–methyl methacrylate (MMA) copolymers was carried out in dioxane/water solution. Four different MF–MMA copolymers with MF mole fractions of 0.225, 0.368, 0.494, and 0.663 were used. The influence of polymeric structure on the rate of reaction was examined, and the rate was found to be dependent on the content of MF units and increased with increasing mole fraction of the MF unit at temperatures of 60, 70, and 80 °C. From infrared analysis, it was found that at low conversion the intensity of an acid fluoride band decreased quickly, while that of the MMA ester band remained unchanged and a carboxylic acid band was absent. The pseudo-first-order rate constants were closely related to the number fraction of (MF–MF) dyads in the copolymers. On the basis of these findings, it is concluded that the hydrolysis occurred at the (MF–MF) configurations, followed by the anhydride formation.

This study is part of our ongoing effort to develop appropriate drug–polymer sustained-release systems for the prevention and prophylaxis of various dental problems. To a greater extent, these systems are based on drugs and other agents covalently bound to polymers, and the release of the agent is generally through a hydrolytic mechanism.

It is well-known that fluoride combats tooth decay by the interaction of fluoride ions with the tooth structure, by interfering with the growth and metabolism of acid-forming bacteria in plaque, or by inhibiting the formation of polysaccharides. Today, teeth are treated with fluoride using fluoridated drinking water, toothpaste, dentifrice, or mouthrinse to increase the resistance of teeth to decay. Some of the dental cements and cavity liners for the restoration of diseased teeth and some of the dental fissure sealants for the purpose of dental caries prevention contain fluoride compounds that are released upon use. The most widely used fluoride compounds added to the above dental

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Table I
Conditions and Results of the Copolymerization of MF (M_1) with MMA (M_2) in Benzene[a]

copolymer designation	initial mole fraction of MF	% conversion	% F in polymer[b]	mole fraction of MF units in polymer
2	0.192	15.6	4.39	0.225
4	0.403	11.6	7.31	0.368
6	0.602	17.8	9.97	0.494
8	0.799	17.0	13.67	0.663

[a] Reaction temperature, 60 °C; initiator, AIBN (0.5 wt %). [b] Determined by fluoride ion analysis following complete hydrolysis in NaOH.

materials are sodium fluoride,[1] stannous fluoride,[2] and amine fluorides.[3] However, these inorganic compounds suffer from the disadvantages that they are poorly soluble in monomers and that it is usually difficult to control the fluoride ion release rate when they are employed. Copolymers of MF and MMA are soluble in MMA monomer, indicating that these copolymers can be mixed with dental resins to provide compatible materials. The results of the hydrolysis study indicate that the copolymers can be utilized as sources of fluoride ion.[4]

In a preliminary report,[4] the synthesis and hydrolytic behavior of methacryloyl fluoride (MF)–methyl methacrylate (MMA) copolymers have been reported. The rates of hydrolysis of the acid fluoride containing copolymers were found to be significantly affected by the copolymer composition. It appeared that the incorporation of MMA units into the polymer reduced their susceptibility to hydrolysis. It is the purpose of the present paper to report some results concerning the rate of hydrolysis of acid fluoride groups in a homogeneous solution in order to establish its rate dependence on chemical composition.

Copolymers having MF mole fractions of 0.225, 0.368, 0.494, and 0.663 were used for the hydrolysis studies at temperatures of 60, 70, and 80 °C. The rate of the reaction and the changes in the copolymer structures were followed by fluorine analysis, using a fluoride electrode, and by infrared spectroscopy. The initial rates of hydrolysis and the rate constants were determined, and the mechanism of hydrolysis is discussed.

Experimental Section

The preparation of MF–MMA copolymers has been described in detail in a previous paper.[4] Four different MF–MMA copolymers having MF mole fractions of 0.225, 0.368, 0.494, and 0.663 were used, and the conditions and the results of the copolymerizations are summarized in Table I.

Hydrolysis of MF–MMA Copolymers. Hydrolysis of the copolymers was carried out in a 90:10 (v/v) mixture of dioxane and a buffered aqueous solution at 60, 70, and 80 °C. A buffer solution of pH 7.0 at 20 °C was prepared by mixing two parts of a 0.1 N disodium hydrogen phosphate solution with one part of a 0.1 N potassium dihydrogen phosphate solution. Each copolymer was first dissolved in redistilled dioxane and then the phosphate buffer solution was added to the dioxane solution. For all experiments the acid fluoride concentration was kept constant at 1.25×10^{-4} mol L^{-1}. A glass tube containing 2.5 mL of the copolymer solution was sealed off and heated for a prescribed time. After a designated heating time, 10 mL of a total ionic strength adjustment buffer solution (TISAB) was added to the cooled reaction mixtures and this was diluted with distilled water until the total volume of solution was 25 mL. The TISAB solution contains acetic acid (5.7 wt %), sodium chloride (5.8 wt %), and sodium citrate (0.03 wt %) and is adjusted to a pH of 5.5 with a sodium hydroxide solution. The degree of hydrolysis was determined by measuring the fluoride ion concentration in the above mixture with a combination fluoride electrode (Toa Electronics Model F-125) coupled with a Toa Electronics Model HM-20B pH/mV meter. The degree of hydrolysis was calculated from millivolt vs. fluoride ion concentration calibration curves. During the measurements, the mixture was held at 20 °C and 10 min was allowed after each immersion of the electrode to attain equilibrium. Further hydrolysis during the fluoride analysis at 20 °C was negligible, since the copolymers were precipitated from the solution by dilution with TISAB.

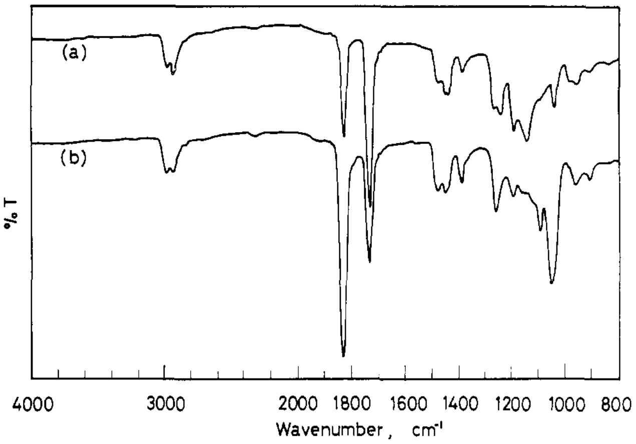

Figure 1. Infrared spectra (film) of copolymer 2 (a) and copolymer 8 (b).

Infrared Analysis. All of the infrared spectra of the copolymer films were obtained with a Hitachi Model 285 infrared spectrophotometer. Films of copolymers 2, 4, 6, and 8 were prepared on glass plates with a dry film thickness of ca. 5 μm. For the hydrolyzed copolymers, the reaction solution was evaporated to dryness below 20 °C and the residue was dissolved in chloroform. Each film of the reacted polymers was prepared by evaporation of the chloroform solution on NaCl or KBr plates.

Results and Discussion

The acid fluoride containing copolymers 2, 4, 6, and 8 (Table I) were prepared by the copolymerization of methacryloyl fluoride (MF) with methyl methacrylate (MMA) in benzene at 60 °C, using AIBN as the initiator. The four different copolymers obtained have good film-forming properties and are soluble in organic solvents such as chloroform, dioxane, benzene, and MMA but insoluble in aliphatic hydrocarbons, ether, and water.[4] These copolymers are stable and degradation was not observed by infrared spectroscopy when the copolymers had been stored at 4 °C for 1 year.

Figure 1 shows the infrared spectra of copolymer 2, which is rich in MMA units, and copolymer 8, which is rich in MF units. The infrared absorption profiles for copolymers 4 and 6 were intermediate between these two extremes. The infrared spectra exhibit strong absorption bands at 1735 and 1829 cm^{-1}, which are attributable to the C=O stretching vibrations of esters and acid fluorides, respectively. With increasing mole fraction of MF units in the copolymers, the absorption at 1829 cm^{-1} increases and the absorption at 1735 cm^{-1} decreases. The absence of absorption bands ascribed to carboxylic acid or anhydride groups demonstrates that no hydrolysis took place during polymerization and the subsequent isolation of copolymers.

Hydrolysis of MF–MMA Copolymers. Hydrolysis of MF–MMA copolymers was carried out in a 90:10 (v/v) mixture of dioxane and a buffered aqueous solution of pH 7.0. These copolymers were expected to provide fluorine-releasing compounds and, therefore, a buffer solution of pH 7.0 was used to simulate the pH of saliva. Because of the insolubility of the MF–MMA copolymers in water, a mixture of dioxane and water was used as solvent to provide a homogeneous hydrolysis system. Hydrolysis of the acid fluoride group in the copolymers was followed by

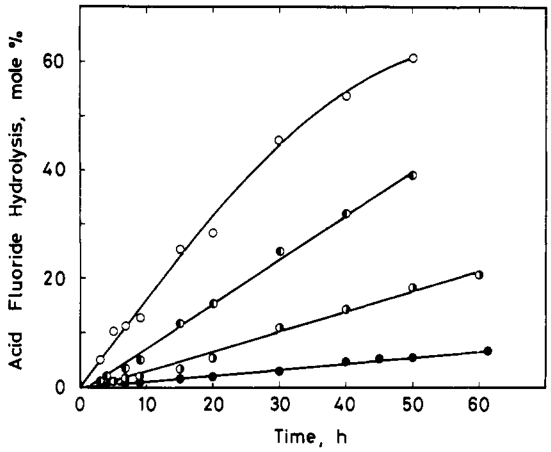

Figure 2. Hydrolysis of MF units in the MF–MMA copolymers at 60 °C: (●) copolymer 2; (◑) copolymer 4; (◐) copolymer 6; (○) copolymer 8.

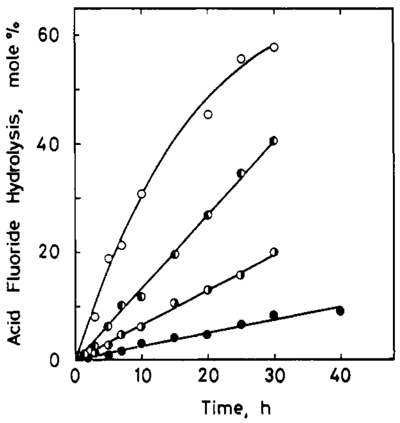

Figure 3. Hydrolysis of MF units in the MF–MMA copolymers at 70 °C: (●) copolymer 2; (◑) copolymer 4; (◐) copolymer 6; (○) copolymer 8.

the determination of fluoride ions with a pH/mV meter, using a constant initial concentration of acid fluoride units (1.25×10^{-4} mol L^{-1}). At 37 °C, the rate was found to be very slow: even after 24 h of reaction, less than 1 mol % of the MF units in copolymer 8 had hydrolyzed and the amount of fluoride ion liberated on hydrolysis of copolymer 2 was within experimental error. Kinetic measurements of the hydrolysis, therefore, were carried out at elevated temperatures of 60, 70, and 80 °C, instead of 37 °C as in the previous case.[4] The glass transition temperature of the copolymers as measured by DSC, was found to be above 90 °C. These findings indicate that the data at the three temperatures may be extrapolated directly to obtain the rate constants at 37 °C, which can be used for more meaningful correlations and comparisons.

The relationship between the degree of acid fluoride hydrolysis and time is shown in Figures 2–4. The susceptibility of MF groups to hydrolysis increases with increasing MF content of the copolymer, i.e., copolymer 2 < copolymer 4 < copolymer 6 < copolymer 8, for all experiments, in spite of the definite initial concentration of acid fluoride units. The initial rates of hydrolysis, R, were calculated from the slope of mole percent of hydrolysis–time curves at time $t = 0$, and the results are summarized in Table II. Rate constants were determined by plotting $\log a/(a - y)$ as a function of time t, where a is the initial acid fluoride concentration and y is the concentration of acid fluoride hydrolyzed at time t. First-order rate plots were linear for the reactions of 60 and 70 °C and linear for at least 50% of the hydrolysis at 80 °C. The slope indicates the corresponding pseudo-first-order rate constant, k_1, and these results are given in Table II. The energy of activation was calculated from the R values at various temperatures: 16 kcal mol^{-1} for copolymer 2, 15 kcal mol^{-1} for copolymer 4, 14 kcal mol^{-1} for copolymer 6 or 8. From these results it is evident that the rate of hydrolysis of acid fluoride groups, that is, the rate of fluoride ion release, is dependent not only on the overall content of MF units in the copolymer but also on the configuration of the copolymer.[4,5]

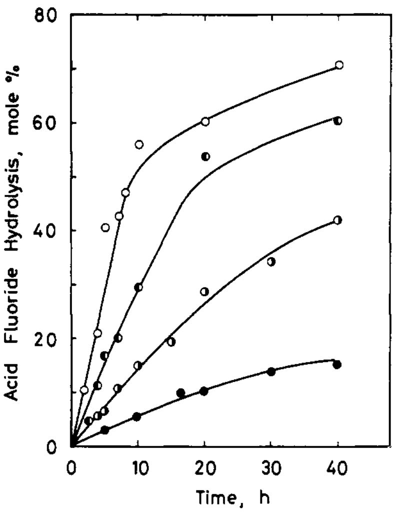

Figure 4. Hydrolysis of MF units in the MF–MMA copolymers at 80 °C: (●) copolymer 2; (◑) copolymer 4; (◐) copolymer 6; (○) copolymer 8.

Table II
Initial Rates of Hydrolysis, R, and Pseudo-First-Order Rate Constants, k_1, of the MF-MMA Copolymers[a]

copolymer designation	temp, °C	10^8R, mol L^{-1} s^{-1}	10^6k_1, s^{-1}
2	60	0.42	0.15
2	70	0.90	0.32
2	80	1.73	0.45
4	60	1.41	0.33
4	70	2.29	0.91
4	80	4.92	1.64
6	60	3.16	1.38
6	70	4.70	2.39
6	80	10.77	5.26
8	60	5.86	2.31
8	70	11.04	3.42
8	80	20.16	10.44

[a] The initial amounts of the copolymers added to the hydrolysis solutions were adjusted to provide an initial acid fluoride concentration of 1.25×10^{-4} mol L^{-1} in all cases.

The rates of hydrolysis of methacrylic acid–MMA copolymers have been reported to be affected by the pH of the reaction media; that is, the reaction velocity increased with an increase in the concentration of sodium hydroxide.[6] The hydrolysis conditions employed here, however, were quite mild compared to those of conventional alkaline hydrolysis or acid-catalyzed hydrolysis,[6–8] and an externally catalyzed hydrolysis of the ester groups in MF–MMA copolymers caused by a phosphate buffer would be negligible, even though an internal hydrolysis might be caused by the neighboring carboxylate groups resulting from the hydrolysis of acid fluoride units.[9]

Infrared Spectra of the Hydrolyzed Copolymers. The structures of the reacted polymers were examined by

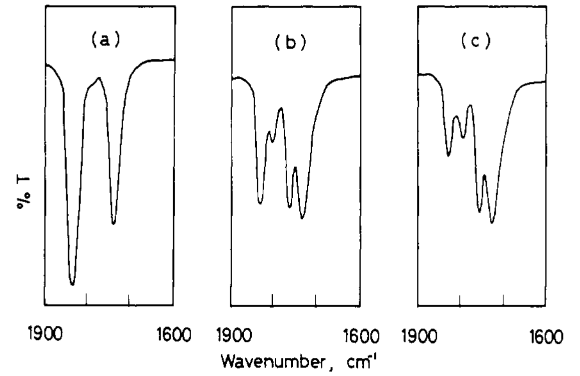

Figure 5. Infrared spectra of copolymer 8 after hydrolysis at 80 °C: (a) before reaction; (b) after 5 h; (c) after 10 h.

Table III
Changes in the Infrared Absorption Intensities of the MF-MMA Copolymers with Time of Hydrolysis at 80 °C

copolymer designation	time, h	rel intens of C=O absorption at[a] 1735 cm^{-1}	1765 cm^{-1}	1803 cm^{-1}	1829 cm^{-1}
2	0	1			0.478
2	20	1	0.013		0.344
2	50	1	0.034		0.243
4	0	1			0.943
4	20	1	0.106	0.016	0.447
4	40	1	0.118	0.020	0.343
6	0	1			1.379
6	10	1	0.264	0.041	0.722
6	20	1	0.309	0.079	0.494
8	0	1			2.451
8	5	1	0.589	0.159	0.860
8	10	1	0.606	0.170	0.399

[a] Intensity relative to the absorption band at 1735 cm^{-1}.

Table IV
Composition and Microstructures for the MF (M_1)-MMA (M_2) Copolymers[a]

copolymer designation	$P_1\{M_1\}$	$P_1\{M_2\}$	$P_2\{M_1M_1\}$
2	0.225	0.775	0.021
4	0.368	0.632	0.087
6	0.494	0.506	0.205
8	0.663	0.337	0.430

[a] $P_1\{M_1\}$ and $P_1\{M_2\}$ are mole fractions of M_1 and M_2 units in the copolymers, respectively.

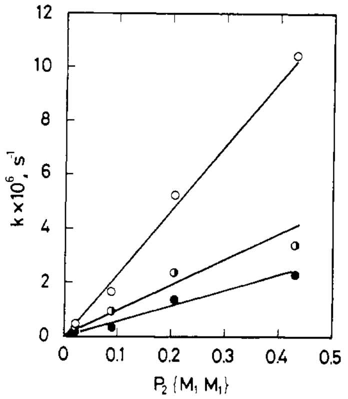

Figure 6. Rate constant k_1 as a function of $P_2\{M_1M_1\}$ for MF (M_1)-MMA (M_2) copolymers. Hydrolysis at (●) 60, (◑) 70, and (○) 80 °C.

infrared spectroscopy. The hydrolyzed copolymers were isolated as films after a given time of reaction at 80 °C, and their infrared spectra exhibited a series of absorption bands in the carbonyl absorption region at 1735, 1765, 1803, and 1829 cm^{-1}. Figure 5 shows the effect of the reaction time on the infrared spectrum of copolymer 8, and the results of the infrared analysis for all copolymers are summarized in Table III. The strong absorption bands at 1735 and 1829 cm^{-1} are due to ester and acid fluoride groups, respectively, and the intensity of the acid fluoride absorption decreased quickly as the reaction proceeded, while the ester (MMA) absorption remained unchanged or changed very little, if at all. Therefore, each ester band was chosen as an internal intensity reference and the other absorptions were normalized relative to the ester absorption (Table III). During the hydrolysis, a pair of new carbonyl absorption bands appeared at 1765 and 1803 cm^{-1}, of which the 1765-cm^{-1} band was the more intense for all hydrolyzed copolymers. These new carbonyl absorptions, 1765 and 1803 cm^{-1}, increased with the reaction time as shown in Table III. In addition, the hydrolyzed products of copolymers 4, 6, and 8 showed a new absorption at 1022 cm^{-1}, and a pronounced shoulder was observed at about 1020 cm^{-1} for copolymer 2 after 50 h of reaction.

Smets et al.[10] have reported that polymers prepared by the cyclopolymerization of methacrylic anhydride show a pair of carbonyl absorption bands at 1760 and 1800 cm^{-1}. Matsuzaki et al.[11] showed that the thermal treatment of poly(*tert*-butyl methacrylate) resulted in the appearance of strong absorptions at 1022, 1760, and 1810 cm^{-1}. These strong absorptions were the result of anhydride group formation. Therefore, the appearance of the new absorption bands at 1022, 1765, and 1803 cm^{-1} in the partially hydrolyzed MF-MMA copolymers indicate the formation of six-membered cyclized anhydride units.[12] A somewhat surprising observation is the absence of the absorption bands of either carboxylic acid or carboxylate groups in the infrared spectra of copolymers isolated in the early stage of the hydrolysis. On the other hand, it is well-known that the anhydride intermediate is formed in the hydrolysis of acrylic acid-acrylamide (or ethyl acrylate) copolymers.[5,9,13] It is, therefore, evident that the methacrylic acid units formed by the hydrolysis of methacryloyl fluoride units readily react with a neighboring acid fluoride, resulting in anhydride formation, and that the anhydride groups are not subject to further hydrolysis.

Mechanism of Hydrolysis. The monomer reactivity ratios for the MF (M_1)-MMA (M_2) copolymerization, $r_1 = 0.41 \pm 0.02$ and $r_2 = 0.62 \pm 0.02$, were obtained by using the Fineman-Ross equation.[4] Since the experimental points appeared to fit the copolymer-monomer composition curve calculated from these values, the copolymerization was considered to proceed according to the terminal model. The distributions of monomer units M_1 and M_2 in the resulting copolymer can be calculated according to the treatment of Ito and Yamashita.[14] The dyad concentration $P_2\{M_1M_1\}$ in copolymers is expressed as

$$P_2\{M_1M_1\} = \frac{r_1x^2}{r_1x^2 + 2x + r_2} \qquad (1)$$

with $x = [M_1]/[M_2]$, where $[M_1]$ and $[M_2]$ are molar concentrations of monomers M_1 and M_2 in the feed. The results of the calculations are given in Table IV. Plots of the experimental rate constants, k_1, against the probability of the (MF-MF) dyad units, $P_2\{M_1M_1\}$, are shown in Figure 6, indicating that the rate constant is closely related to the number fraction of (MF-MF) dyads in the MF-MMA copolymers. Apparently, the rate of hydrolysis of a given MF unit is affected by the configuration of the

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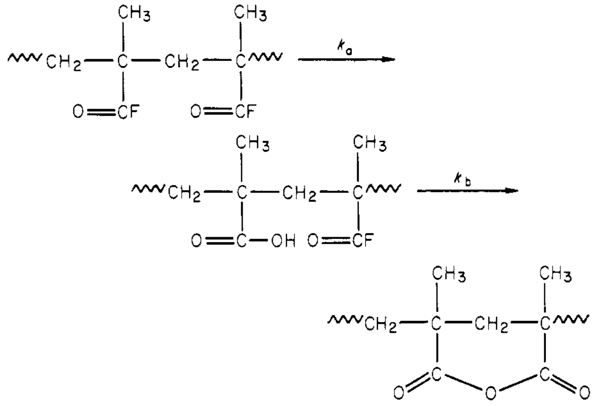
groups proximate to it, and an ester group unfavorably influences the hydrolysis of an adjacent acid fluoride unit. This effect may be a steric one. At a low content of MF units, each MF unit in the MF–MMA copolymer is isolated by MMA units, where the (MMA–MF–MMA) configuration is predominant. The MF units in (MMA–MF–MMA) triads are considered to hydrolyze much more slowly than in the (MF–MF) dyad, since the rate constants were 11–23 times lower for copolymer 2 than for copolymer 8 (Table II).

As mentioned in the preceding section, the hydrolysis of the MF–MMA copolymers involves two mechanisms, an externally catalyzed hydrolysis and an internal hydrolysis with participation of adjacent groups. The results of the infrared measurements indicate that the hydrolysis of MMA units in the early stage of the reaction is practically negligible in comparison to that of the MF units, since the intensities of ester carbonyl bands remained almost unchanged until late in the reaction. Thus, the reaction occurred exclusively at the (MF–MF) configurations. An anhydride formation reaction between different polymeric chains seems unlikely if one considers the dilution of the medium and the solubility of the products in organic solvents. Therefore, the reaction mechanism in the initial stage is formulated as follows:



(2)

The initial hydrolysis of an acid fluoride unit is the rate-determining step in the reaction sequence; i.e., $k_a < k_b$, since any absorption due to carboxylic acid groups was not observed in the infrared spectra of the products at a low degree of hydrolysis.

At a late stage the hydrolyzed copolymers were precipitated, in part, from the reaction mixture, and the hydrolysis rate decreased gradually, giving first-order plots with a downward curvature. The infrared analysis revealed the presence of methacrylic acid units in the products at a high degree of hydrolysis.

It may be concluded that the hydrolysis rate of MF units in the MF–MMA copolymers depends on their respective microstructures, especially on their number fraction of (MF–MF) sequences. The findings suggest that the rate of fluoride ion release from MF–MMA copolymers can be made to vary by changes in their configurations even at a constant content of MF units in the copolymers: the rate would be highest for MF–MMA block copolymer and lowest for MF–MMA alternating copolymer.

References and Notes

(1) Retief, D. H.; Sorvas, P. G.; Bradley, E. L.; Taylor, R. E.; Walker, A. R. *J. Dent. Res.* **1980,** *59,* 573.
(2) Fogels, H. R.; Alman, J. E.; Meade, J. J.; O'Donnell, J. P. *J. Am. Dent. Assoc.* **1979,** *99,* 456.
(3) Ringelberg, M. L.; Webster, D. B.; Dixon, D. O.; LeZotte, D. C. *J. Am. Dent. Assoc.* **1979,** *98,* 202.
(4) Kadoma, Y.; Masuhara, E.; Ueda, M.; Imai, Y. *Makromol. Chem.* **1981,** *182,* 273.
(5) Smets, G.; Van Humbeeck, W. *J. Polym. Sci., Part A* **1963,** *1,* 1227.
(6) Smets, G.; De Loecker, W. *J. Polym. Sci.* **1959,** *41,* 375.
(7) Smets, G.; De Loecker, W. *J. Polym. Sci.* **1960,** *45,* 461.
(8) Glavis, F. J. *J. Polym. Sci.* **1959,** *36,* 547.
(9) Smets, G. *Angew. Chem.* **1962,** *74,* 337.
(10) Smets, G.; Hous, P.; Deval, N. *J. Polym. Sci., Part A* **1964,** *2,* 4825.
(11) Matsuzaki, K.; Okamoto, T.; Ishida, A.; Sobue, H. *J. Polym. Sci., Part A* **1964,** *2,* 1105.
(12) Sakurada, I.; Iwagaki, T.; Sakaguchi, Y. *Kobunshi Kagaku* **1964,** *21,* 270.
(13) Chapman, C. B. *J. Polym. Sci.* **1960,** *45,* 237.
(14) Ito, K.; Yamashita, Y. *J. Polym. Sci., Part A* **1965,** *3,* 2165.

Tensile and Swelling Behavior of Model Silicone Networks with Low Extents of Cross-Linking

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ABSTRACT: Multifunctional elastomeric networks of known network chain density, ν_s/V, were prepared by end-linking α,ω-divinyl-poly(dimethylsiloxane) (α,ω-divinyl-PDMS) chains ranging in number-average molecular weight from 9320 to 28100 with poly(methylsiloxane) (PMHS) of average intrinsic functionality 43.9. The fraction of silane vinyls reacted, ϵ, as measured from sol fraction analysis, varied from 0.95 to 0.4. The stress–strain isotherms in elongation and the swelling ratios in benzene were measured at 25 °C for these networks. Network chain densities calculated from these measurements exceeded the values predicted from stoichiometry. These excesses diminished with decreasing ϵ. Molecular theories presuming a contribution from trapped entanglements to the small-strain modulus gave good agreement with the data and offered a reasonable explanation of the trends observed.

In previous papers,[1,2] the equilibrium tensile behavior of model silicone elastomeric networks with high junction functionalities was described. Such high-functionality networks were prepared by reacting the terminal vinyl groups on α,ω-divinyl-poly(dimethylsiloxane) (α,ω-divinyl-PDMS) chain molecules with the silane hydrogens on poly(methylsiloxane) (PMHS):

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