

DETERMINATION OF THE TACTICITY OF POLY(METHYL METHACRYLATE) BY HYDROLYSIS RATE MEASUREMENTS

František MIKEŠ and Jan PECKA

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, 162 06 Prague 6*

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The rate of hydrolysis of poly(methyl methacrylate) increases with the content of meso(isotactic) diads in the polymer. The increase in the rate of hydrolysis of isotactic polymers is due to an intramolecular nucleophilic attack by the adjacent carboxylic ion on the carbonyl carbon atom in the ester group. An analysis of the content of sequences of variously arranged ester and carboxylic groups shows that the hydrolysis of *s*-poly(methyl methacrylate) is a random process, while *i*-poly(methyl methacrylate) is hydrolyzed gradually (by zip mechanism), starting from the carboxylate group formed by an external attack by hydroxylic ions. The kinetic data thus obtained cannot be interpreted in terms of a simple kinetic model. The tacticity of poly(methyl methacrylate) may be estimated from the dependence of the rate of hydrolysis on the content of meso diads determined by NMR spectrometry. The rate of hydrolysis depends not only on the tacticity of the polymer, but probably also on its configurational sequence statistics.

The hydrolysis¹ and hydrazinolysis² of the ester group in poly(methyl methacrylate) (PMMA), and in some cases also aminolysis³ are in fact the only feasible polymer-analogous reactions of PMMA. The other reactions of the ester group in PMMA, e.g. reesterification, do not proceed at a measurable rate. Hence, hydrolysis of the ester group is usually the first step in chemical modifications of PMMA, e.g. in the labelling of stereoregular PMMA by using the fluorescence, spin or some other signal group.

It has been shown in several studies that the rate of hydrolysis of the ester group of the methyl methacrylate constitutional unit is affected by the side group in the adjacent constitutional polymer unit. Morawetz et al.⁴ found that the hydrolysis of *p*-nitrophenyl methacrylate units in copolymers of *p*-nitrophenyl methacrylate with acrylic acid is accelerated by the presence of adjacent carboxylate groups. Smets et al.⁵ observed that the hydrolysis of copolymers of acrylamide and acrylic acid is accelerated by undissociated carboxylic groups. Similarly, the hydrolysis of copolymers of methyl methacrylate and methacrylic acid is affected by the adjacent carboxylate and carboxylic function⁶⁻⁸. It has been reported that adjacent cyclic anhydride groups arising during the acid hydrolysis of PMMA may influence the extent of the reaction⁹. A number of papers are dealing with the effect of the presence

and size of the functional group on the process of hydrolysis of other homopolymers and copolymers¹⁰⁻¹⁵.

All that has been said above indicates that the rate of hydrolysis depends on the tacticity of PMMA; however, only little attention has been devoted to the extent of the influence, especially with respect to the type of tacticity. This study is focussed on a detailed investigation of the dependence of the hydrolysis of PMMA on its tacticity. Using the relations thus obtained, the tacticity of the polymer can be estimated from the rate of hydrolysis.

EXPERIMENTAL

Preparation of Poly(methyl methacrylate) (PMMA)

Radical polymerizations of methyl methacrylate (MMA) were carried out in 1,4-dioxane solutions (20 wt. % monomer, 0.4 wt. % initiator) at 20–200°C in sealed ampoules (prior to sealing, oxygen dissolved in the reaction mixture was removed by bubbling with nitrogen). Isotactic polymers were prepared by solution polymerizations of MMA in toluene (1.5 mol l⁻¹) with tert-butylmagnesium bromide¹⁶ (30 mmol l⁻¹), butylmagnesium bromide (120 mmol l⁻¹), or lithium tert-butoxide¹⁷ (3.0 mol l⁻¹ of monomer, 22.6 mmol l⁻¹ of initiator) as initiators. Syndiotactic polymers were prepared by the polymerization of MMA in toluene (0.83 mol l⁻¹) initiated with the system¹⁸ (CH₃CH₂)₃Al–TiCl₄ (molar ratio Al/Ti = 5.0, [Ti₄Cl] = 33 mmol . l⁻¹); the fresh suspension of the Ziegler–Natta system in toluene was kept at 0°C for 30 min before the application.

The polymerizations were terminated by the addition of methanol (in the case of a complex coordination polymerization acidified with hydrochloric acid); the polymers were reprecipitated into methanol or hexane several times and dried at reduced pressure (70 Pa).

The other reaction conditions, the radical initiators used and characterization of the polymers obtained are summarized in Table I.

Hydrolysis of PMMA

The hydrolysis took place at 85°C in sealed ampoules or in a stainless steel autoclave (Büchi Ingenieur-bureau SFS Zürich). To a solution of the polymer in 1,4-dioxane (31.25 g of polymer per one litre of 1,4-dioxane), a methanolic solution of potassium hydroxide (500 ml of a solution of 20% potassium hydroxide per one litre 1,4-dioxane)¹⁹ was added, and the reaction mixture was bubbled through with nitrogen. The reaction mixture was sampled during the reaction time (reaction in the autoclave). The polymer was precipitated into water acidified with hydrochloric acid in excess. The partly hydrolyzed polymer was removed by filtration, thoroughly washed with water to neutral reaction, and dried (four days at room temperature and 70 Pa). At the same reaction time, the content of carboxylic groups in the polymers was the same in both the experiments carried out in ampoules and those which took place in the autoclave. A GPC analysis of the samples before and after the hydrolysis showed that during the hydrolysis no degradation of the polymers takes place.

Characterization of the Polymers

The content of carboxylic groups in the polymer (molar fraction, x_{COOH}) was determined by titrating the sample (0.1–1.2 g) in 1,4-dioxane (30 ml) with methanolic 0.05M-CH₃ONa using

phenolphthalein. For polymers hydrolyzed to a higher degree ($\sim 40\%$), x_{COOH} was determined also by ^1H NMR spectrometry (spectra recorded in pentadeuteriopyridine at 100°C in a Bruker 400 AC apparatus, hexamethyldisiloxane as the standard) using the relation

$$x_{\text{COOH}} = 1 - [5I_{\text{OCH}_3}/3(I_{\text{CH}_3} + I_{\text{CH}_2})] \quad (1)$$

in which I_{OCH_3} , I_{CH_3} , and I_{CH_2} are areas below the resonance intensity peaks of carbomethoxy, α -methyl, and β -methylene protons, respectively.

The tacticity of the polymers was determined by ^1H NMR spectrometry in a solution (10 wt. % polymer) in *o*-dichlorobenzene or deuteriochloroform at 150° or 60°C using the same apparatus. The signals of α -methyl protons²⁰ for *i*-, *h*-, and *s*-triads lie at 1.33, 1.21, and 1.10 ppm, respectively. The NMR spectra of partly hydrolyzed polymers were recorded in pyridine or pentadeuteriopyridine at 100°C . The chemical shifts of α -methyl protons in the polymers obtained by the partial hydrolysis of syndiotactic PMMA for various triads were²¹: AAA 1.01, ABA 1.14, AAB 1.23, ABB 1.37, BAB 1.48, BBB 1.61 ppm. (A is the methyl methacrylate monomeric unit, B is the methacrylic acid monomeric unit).

The number (\bar{M}_n) and mass (\bar{M}_w) average molar mass of the polymers was determined by GPC in tetrahydrofuran using a Hewlett-Packard 1090 apparatus. The automatic analysis process was controlled by an HP 85B personal computer. The columns used were PL gel $10\ \mu$ MIXED or PL gel $10\ \mu$ 500 (Polymer Laboratories LTD, Shropshire, U.K.). The apparatus was

TABLE I

Conditions of preparation and characterization of polymers (PMMA). Initiators: ABIN 2,2'-azo-bis(2-methylpropionitrile), ABVN 2,2'-azo-bis(2,4-dimethyl-4-methoxyvaleronitrile), CH 7-cumenyl hydroperoxide. Symbols: T polymerization temperature, t_p polymerization time, \bar{M}_n and \bar{M}_w molar masses, *i*, *h*, *s* content of isotactic, heterotactic, and syndiotactic triad, respectively, P_m fraction of meso (isotactic) diads

Polymers	Initiation system	T $^\circ\text{C}$	t_p h	$\bar{M}_n \cdot 10^{-3}$ $\bar{M}_w \cdot 10^{-3}$		Tacticity, %			P_m
				g mol ⁻¹		<i>i</i>	<i>h</i>	<i>s</i>	
<i>s</i> -PMMA-1	$\text{Et}_3\text{Al-TiCl}_4$	-78	0.7	87	206	4.2	10	86	0.09
<i>s</i> -PMMA-2	$\text{Et}_3\text{Al-TiCl}_4$	-78	7	120	182	3.4	10	87	0.097
<i>s</i> -PMMA-3	$\text{Et}_3\text{Al-TiCl}_4$	-78	9	134	250	5.2	8	87	0.09
PMMA-20	ABVN	~ 20	48	210	829	2.2	30	68	0.17
PMMA-60-1	ABIN	60	3	287	688	4.0	33	63	0.20
PMMA-60-2 ^a	ABIN	60	6	477	968	4.4	33	63	0.21
PMMA-120	CH	120	3.3	265	852	6	39	55	0.26
PMMA-150	CH	150	2	300	1 052	7	42	51	0.28
PMMA-200	CH	200	2.5	36	121	9	41	50	0.29
<i>i/s</i> -PMMA-30 ^b	BuMgBr	-30	24	25	269	56	18	26	0.65
<i>i/s</i> -PMMA-78 ^b	BuMgBr	-78	24	31	323	66	15	19	0.73
<i>i</i> -PMMA-1	<i>t</i> -BuOLi	~ 20	16	96	277	74	15	11	0.82
<i>i</i> -PMMA-2	<i>t</i> -BuMgBr	-78	24	6.1	10.2	85	10	5.4	0.89

^a Concentration of initiator 0.15 wt. %. ^b Unreliable values — stereocomplexes are formed.

calibrated using monodisperse poly(methyl methacrylate) fractions ($\overline{M}_w/\overline{M}_n < 1.05$) (Polymer Standard Service, Mainz, F.R.G.). The experimental data were evaluated by means of the software supplied by the firm.

RESULTS AND DISCUSSION

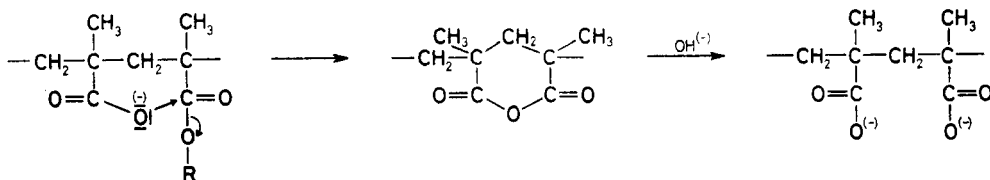
Poly(methyl methacrylates) with various tacticity and molar mass were obtained by the radical, anionic and Ziegler–Natta-system initiated polymerization (Table I). All polymers thus prepared (PMMA) were hydrolyzed under the same conditions with potassium hydroxide in a 1,4-dioxane–methanol mixed solvent. The reaction took place in an approximately sevenfold molar excess of potassium hydroxide. The dependence of the degree of reaction transformation expressed by the fraction of carboxylic groups in the polymer (in mole %) on time for polymers of various tacticity and molar mass can be seen in Fig. 1.

The rate of hydrolysis increases with the content of isotactic triads in the polymer. The dependence of the rate of hydrolysis on the content of meso diads in the polymer is illustrated in Fig. 2.

The effect of tacticity on the rate of alkaline hydrolysis of poly(methyl methacrylate) has been observed by Glavis²², who showed that polymers obtained by radical polymerization and the syndiotactic polymer (*s*-PMMA) are hydrolyzed relatively slowly, while the isotactic polymer (*i*-PMMA) is hydrolyzed very fast.

Later, these observations were confirmed by Smets and De Loecker⁷ who used quantitative results concerning the rate of hydrolysis of copolymers methacrylic acid–methyl methacrylate of approximately the same chemical composition, but different tacticity. In all these cases the increase in rate of hydrolysis of isotactic polymers was explained by an intramolecular nucleophilic attack by the adjacent carboxylic ion on the carbonyl carbon atom of the ester group (Scheme 1). The attack is accompanied by the formation of a six-membered anhydride intermediate; the formation of the cyclic intermediate determines the reaction rate⁴.

In the case of poly(methyl methacrylate) no carboxylic groups are present in the polymer at the beginning. This is why at the beginning of the reaction in a strongly basic medium the carbonyl carbon atom is externally attacked by hydroxylic groups.



SCHEME 1

Only after that an intramolecular attack on the ester group by the adjacent carboxylate ion becomes feasible.

In the case of the acid catalyzed hydrolysis of poly(*N,N*-dimethylacrylamide)¹¹ the initial stage of hydrolysis could be described in terms of the relation

$$dx/dt = k_1(a - x) + k_2Cx \quad (2)$$

here, a is the initial concentration of ester groups, x is the concentration of carboxylic

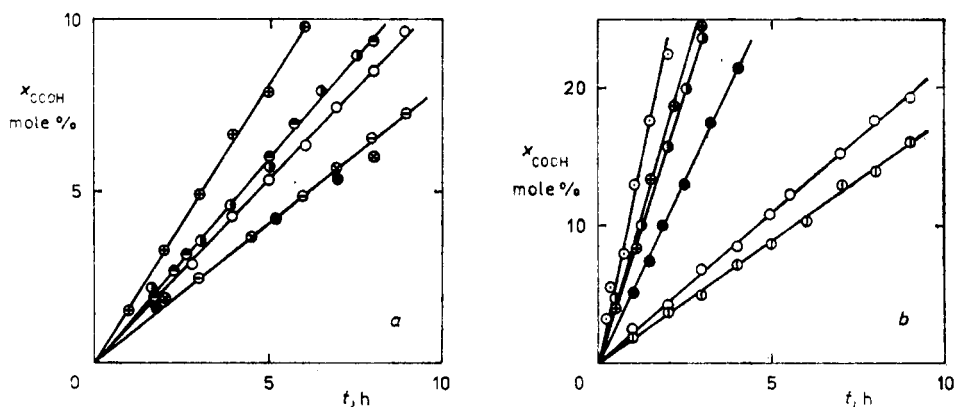


FIG. 1

Dependence of the content of carboxylic groups in the polymer (PMMA), x_{COOH} , on the time of hydrolysis: *a* \ominus *s*-PMMA-1, \bullet *s*-PMMA-2, \otimes *s*-PMMA-3, \circ PMMA-20, \ominus PMMA-60-1, \oplus PMMA-60-2, \oplus PMMA-120; *b* \circ PMMA-150, \circ PMMA-200, \bullet *i/s*-PMMA-30, \ominus *i/s*-PMMA-78, \oplus *i*-PMMA-1, \circ *i*-PMMA-2

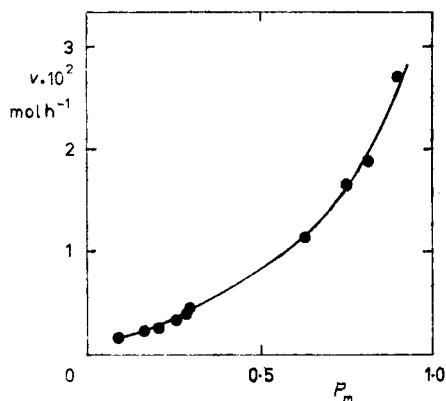


FIG. 2

Dependence of the rate of hydrolysis of PMMA, v , on the fraction of meso(isotactic) diads, P_m , in PMMA

groups at a time t , k_1 , k_2 are the rate constants for the intermolecular and intramolecular reaction respectively, and the constant C is defined as the fraction of the isotactic (m) or syndiotactic (r) sequences, depending on the fact which sequence meets steric requirements for the intramolecular reaction; with respect to the conformational stability of 1,3-disubstituted six-membered rings, in this case we have the isotactic configuration.

The dependence of the content of carboxylic groups on the reaction time (Fig. 1) is linear for all polymers up to 20% of the reaction transformation. Our experimental data cannot be correlated using Eq. (2), however. As has been demonstrated above, in the alkaline hydrolysis of PMMA the effect of the adjacent group is more or less operative, as proved by determination of the composition statistics of polymers formed after the hydrolysis. The content of the individual sequences of ester and carboxylic groups in these polymers may be determined from the NMR spectra for s -PMMA and i -PMMA:

s-Poly(methyl methacrylate). Due to the fact that, in s -PMMA, only one type of configurational triads is possible, the splitting of protons of the α -methyl group

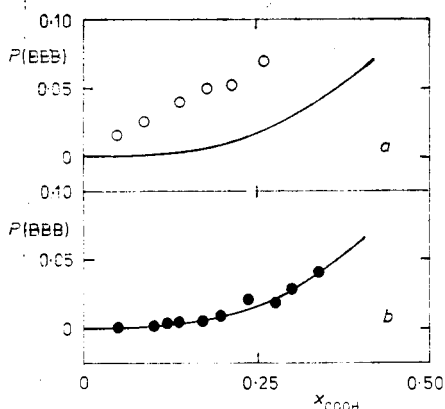


FIG. 3

Dependence of the probability of occurrence of BBB triads in partly hydrolyzed i -PMMA (a) and s -PMMA (b), $P(\text{BBB})$, on the molar fraction of carboxylic groups in the polymer, x_{COOH} ; curves illustrate a random process of hydrolysis

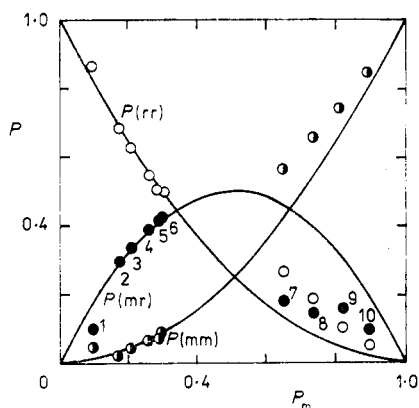


FIG. 4

Probability P of isotactic (mm), heterotactic (mr) and syndiotactic (rr) triads in PMMA as a function of the fraction of meso(isotactic) addition during propagation, P_m : 1 s -PMMA-1, 2 PMMA-20, 3 PMMA-60, 4 PMMA-120, 5 PMMA-150, 6 PMMA-78, 200, 7 i/s -PMMA-30, 8 i/s -PMMA-78, 9 i -PMMA-1, 10 i -PMMA-2; \bullet mm , \circ mr , \circ rr triads; curves illustrate a random propagation process

of partly hydrolyzed *s*-PMMA can be attributed to the composition of these triads or higher sequences. The content of the triads BBB, BAB, and BBA was determined from an analysis of the NMR spectra of *s*-PMMA hydrolyzed to various degrees. Figure 3 shows that the alkaline hydrolysis of *s*-PMMA proceeds randomly. The probability (P) of the occurrence of BBB triads calculated from experimental data coincides with the probability calculated for a random process.

i-Poly(methyl methacrylate). Similarly to *s*-PMMA, the splitting of signals of protons of the α -methyl group in *i*-PMMA is due to the arrangement of the ester or carboxylic group in isotactic triads. A preliminary analysis of several samples of *i*-PMMA hydrolyzed to various degrees has revealed that the probability of occurrence of triads of carboxylic groups is much higher than it should be for a random process of hydrolysis. Assignments of the signals and a complete description of the microstructure of partly hydrolyzed *i*-PMMA are being investigated. The higher content of triads of carboxylic groups in *i*-PMMA hydrolyzed to a low degree proves that hydrolysis of this polymer proceeds predominantly via the intramolecular mechanism. As a consequence, the carboxylate groups inside these sequences do not take an active part in the intramolecular mechanism of hydrolysis, and its course cannot be described in terms of Eq. (2), even at a low degree of conversion.

The tacticity of PMMA (fraction of *m* diads) can be estimated from the dependence of the rate of hydrolysis (carried out under the same conditions) on the tacticity of PMMA determined by NMR spectrometry (Fig. 2).

The initial rate of alkaline hydrolysis of poly(methyl methacrylate) obviously depends to some extent also on the configurational statistics of sequences of the polymers prepared in this study. The sequence statistics of the polymers obtained by radical polymerization corresponds to a random process of the addition of the monomer to the propagating polymeric radical, while polymers obtained by the anionic and complex coordination polymerization have a higher content of isotactic and syndiotactic sequences, i.e. are of a partly block character (Fig. 4).

A more detailed quantitative analysis of experimental data obtained in the hydrolysis of poly(methyl methacrylates) of various tacticity and configurational sequence statistics will be dealt with in a forthcoming study.

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