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KINETIC INVESTIGATIONS OF REACTIONS WITH MALEIC ANHYDRIDE COPOLYMERS AND MODEL COMPOUNDS

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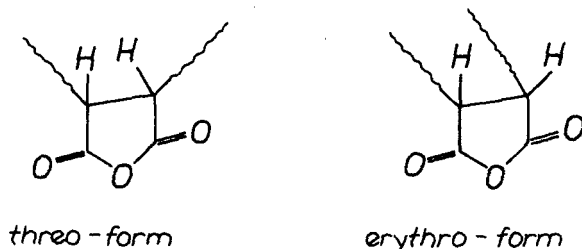
Technische Hochschule Leuna-Merseburg
DDR 4200 Merseburg, German Democratic Republic

ABSTRACT

Alternating copolymers that contain maleic anhydride (MAn) as a component occur in two different stereochemical configurations which are differentiated by their reactivity. Model compounds, 2,3-dialkylsuccinic acids and their anhydrides, were investigated and it was demonstrated that there is a distinct difference between *threo* and *erythro* configurations in their chemical and physical behavior. Both configurations also occur in the alternating copolymers. Beside the model compounds, the alternating copolymers ethylene-MAn, propylene-MAn, and styrene-MAn were investigated in their reactions with amines, alcohols, and water (hydrolysis). The *cis* configurations showed the higher reaction rates. Reactions of the anhydride moieties with equimolar amounts of aniline, ethanol, and water demonstrated that reactions follow second-order rate laws. With excess reactant, the reaction follows a pseudo-first-order rate law. The rate constants depend on the degree of polymerization and on the comonomer. Increasing steric hindrance and molecular weight lead to a decrease of the reaction rate. Catalysis of the hydrolysis reaction by tertiary amines results in similar rate constants for the configurations of the substituted succinic acid anhydrides. The reasons are discussed.

INTRODUCTION

Alternating copolymers of maleic anhydride (MAN) are gaining more and more importance in industry as auxiliary agents. Depending on applications, a large fraction of the MAN copolymers are modified by reactions at the MAN ring. A detailed summary of the application possibilities has been given by Trivedi and Culbertson [1]. Many modifying reactions were reported by Rätzsch [2]. 2,3-Dialkylsuccinic anhydride, which corresponds to the MAN unit in the MAN copolymers, represents a diastereoisomeric compound with different reactivities of the two configurations. From Koenig's and our studies [3, 4], the structure of the MAN units in the polymer molecule is known. The influence of the structure on the reactivity is investigated here by using model compounds and copolymers.



BACKGROUND

2,3-Dialkylsuccinic acids and their anhydrides are diastereoisomeric compounds whose *threo* and *erythro* configurations differ in their physical and chemical properties. We also find both configurations as structural units in alternating MAN copolymers [4].

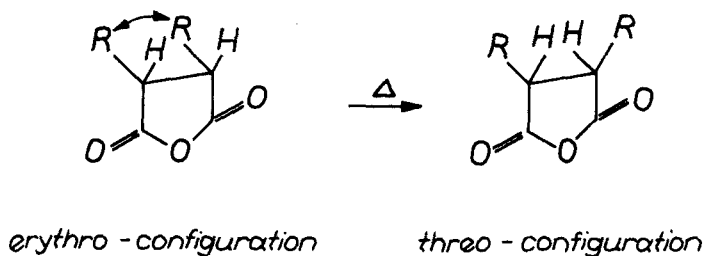
Eberson [5] investigated a series of methyl- and ethyl-substituted succinic anhydrides (SAn) with regard to their hydrolysis rates. In comparison with SAn, the rate constants of the mono- and 2,3-disubstituted methylsuccinic anhydrides are higher, and those of the mono- and 2,3-disubstituted ethylsuccinic anhydrides are smaller. The rate constant of 2,3-dialkylsuccinic anhydrides is 1.5 to 2 times higher for the *erythro* form than for the *threo* form.

Bouvier and Bruneau [6] investigated esterification reactions of hexadecanol-1 with substituted SAn. The rate constant of the *erythro* form of the 2,3-diethylsuccinic anhydride is three times higher than that for the *threo* form.

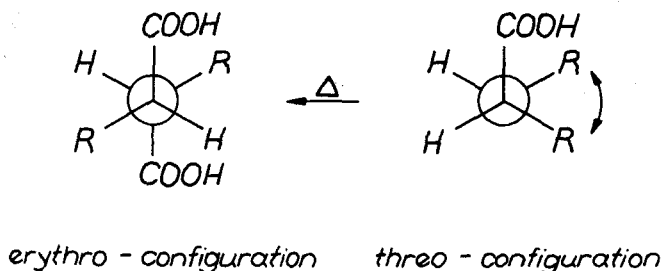
Bode and Brockmann [7] investigated, among others, cyclization and rearrangement reactions of both configurations of 2,3-dialkylsuccinic acids and their derivatives. They found that *erythro* compounds tend to ring fission under hydrolytic conditions far easier than the *threo* compounds, providing support for the statement that *erythro* anhydrides have a higher energy level than the corresponding *threo* compounds because of Pitzer tension [8].

The *erythro* configuration of the 2,3-dialkylsuccinic anhydride is the more reactive configuration for reactions involving opening of the anhydride ring, compared to the *threo* configuration. For reactions with cyclization, the reactivities are reversed. Thus, Bode and Brockmann [7] report that the cyclization of the acids and their monoamides with thionyl chloride is achieved more easily for the *threo* form to build *threo* anhydrides or imides, respectively, than for the *erythro* form.

Linstead and Whalley [9], who investigated the relative stabilities of both configurations of 2,3-dimethylsuccinic acid and the corresponding derivatives, report on the possibility of the rearrangement of the configurations. With the acid and with the diamide, the rearrangement occurs from the *threo* to the *erythro* form, and with the anhydride and the imide from the *erythro* to the *threo* form.



Bode and Brockmann [7] also reported the possibility of rearrangement reactions. For annular derivatives, steric hindrance causes the *threo* configuration to be the more stable one.

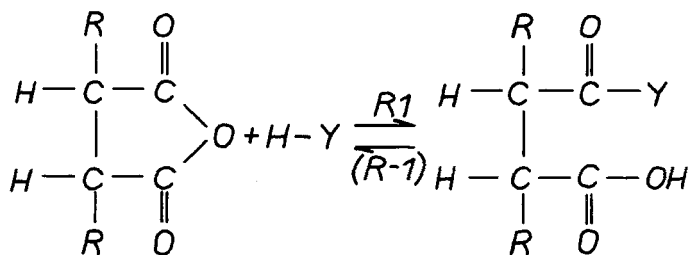


However, in the case of the open-chain derivatives, the *erythro* configuration is the more stable one.

Bromination of the neutral salt of maleic acid produces an *erythro-threo* mixture of the salt of 2,3-dibromosuccinic acid [10]. With decreasing reaction temperature, the *erythro* product is formed preferentially.

In summary, it can be stated that the *threo* configuration is the more stable and thus the preferred configuration of cyclic derivatives of 2,3-dialkylsuccinic acid compounds as, for instance, anhydrides and imides; while it is the *erythro* configuration of the open-chain derivatives as, for instance, acids and amides.

From these results, one may conclude that ring-opening reactions of the cyclic compounds at the *erythro* configuration proceed faster than at the *threo* configuration, and that cyclization reactions of the open-chain compounds show the opposite behavior. Reactions of annular anhydrides with nucleophiles of the type H-Y (H-OH, H-OR, H-NHR), which occurs with fission of the anhydride ring via a carbonyl reaction, proceed by a second-order addition-elimination mechanism.



In the case of H₂O and HO-R the reverse reaction must also be considered, especially at temperatures above 100°C. The monoamide is able to react by ring formation to give the more stable imide. Reactions of this type are, fundamentally, amenable to acidic and basic catalysis. For this reason the catalytic effect of the carboxylic group which is formed during the reaction has to be taken into consideration.

Loucheux and Banderet [11] reported on a strong autocatalytic effect during the reaction of carboxylic acid anhydrides with aryl amines. Bouvier and Bruneau [6] used a substituted SAn for the esterification reaction. In the 160-200°C temperature range, the kinetics for the reversible reaction were second order. When one component is present in excess, the course of the reaction can be described by pseudo-first-order kinetics.

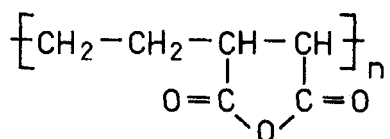
The kinetic relations become more complex for all the mentioned types of reaction if both configurations of the 2,3-dialkylsuccinic acids and their derivatives are present simultaneously during the reaction. This is the case

in a mixture of both configurations but also in reactions of MAn-alkene copolymers which contain both configurations of the SAN units in their chain [4]. This is so because, due to their alternating structure, these copolymers must be considered 2,3-dialkylsuccinic acid derivatives.

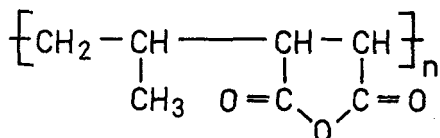
EXPERIMENTAL RESULTS AND DISCUSSION

Succinic anhydride (SAN) and 2,3-diethylsuccinic anhydride consisting of a *threo* (*threo*-2,3-diethyl-SAN contains 20% of the *erythro* configuration) and an *erythro* configuration were used for the following investigations. Three alternating maleic anhydride (MAn) copolymers, i.e., ethene-MAn, propene-MAn, and styrene-MAn, were investigated.

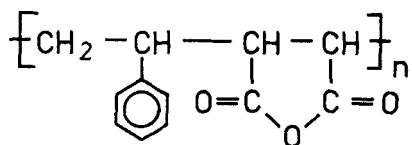
Ethene - MAn - Copolymer



Propene - MAn - Copolymer



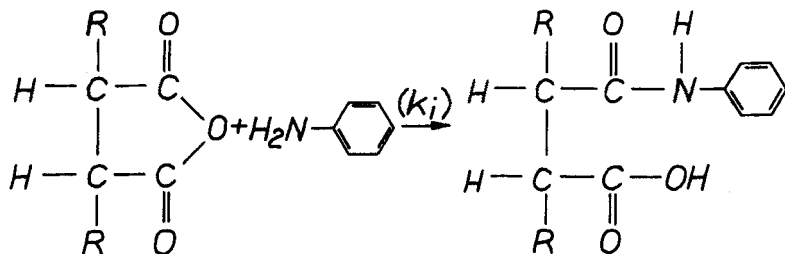
Styrene - MAn - Copolymer



Amidation Reaction with Aniline

Equimolar Reaction Anhydride-Amine

In equimolar reactions of anhydride groups with aniline in dimethylformamide (DMF), an autocatalytic effect of the $-\text{COOH}$ groups being formed was found, as previously described by Loucheux and Banderet [11].



The interpretation of the $(\text{concentration})^{-1}$ vs time curve for the equimolar reaction of SAN and aniline showed that the reaction cannot be interpreted by use of a second-order rate law. An interpretation of the reaction by sections using a second-order time law resulted in a steady increase of k with conversion for the low-molecular compounds (Fig. 1). In contrast, the accelerating effects of the generated carboxyl groups were only noticeable in reactions on propene-MAN copolymers up to about 40% conversion. At higher conversions, k decreases continuously with rising conversion (Fig. 2), as previously demonstrated by Rätzsch and Phien [2].

Two tendencies are superposed during the reaction on the copolymers. One is the autocatalytic effect of the carboxyl groups also being formed during this reaction, and the other is a polymer-specific delay of the reaction which increases strongly with increasing conversion and then predominates. This polymer-specific retardation, as described by Rätzsch and Hue [12], even leads to limited conversion for the equimolar reaction of propene-MAN copolymers with secondary aliphatic amines. Addition of acetic acid to the reaction mixture resulted in a practically time-independent concentration of carboxyl groups.

The interpretation of equimolar reactions of the model compounds with aniline and an excess of acetic acid became possible over the whole range of conversion by using a second-order rate law (Fig. 3). The resulting reaction rates led to the results shown in Table 1.

It was impossible to interpret the equimolar reaction of ethene- and propene-MAN copolymers with aniline and an excess of acetic acid over the

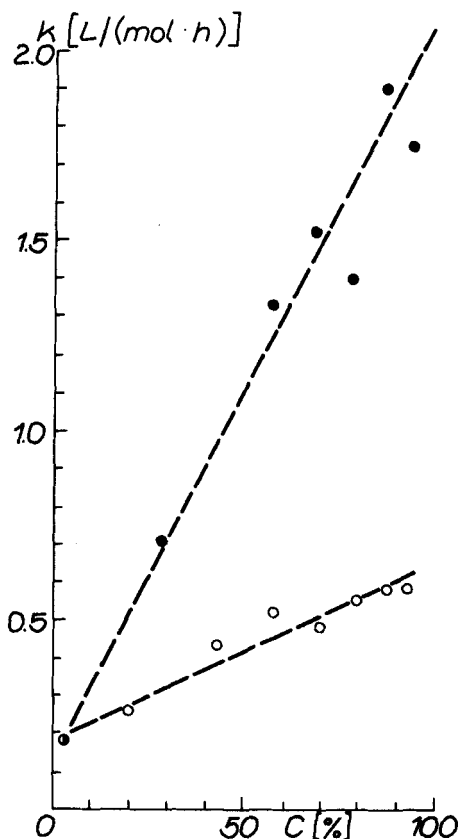


FIG. 1. Reaction of *threo*- (○) and *erythro*- (●) 2,3-diethyl-SAn with aniline in DMF. 298 K. $C_{0,\text{Anhydride}} = C_{0,\text{Amine}} = 0.1 \text{ mol/L}$.

whole range of conversion by a second-order time law. An interpretation by sections in imitation of second order showed a steady decrease of k_j as the reaction progressed (Fig. 4). An extrapolation of the k value to zero conversion resulted in the rate constants shown in Table 2. The relative value of k for the ethene-MAN copolymer of 0.58 is close to the 0.62 value for the *erythro* configuration of its low-molecular analog and significantly larger than the 0.24 value for the *threo* configuration model compound. Investigations of the copolymer structures by ^{13}C -NMR spectroscopy [4] showed

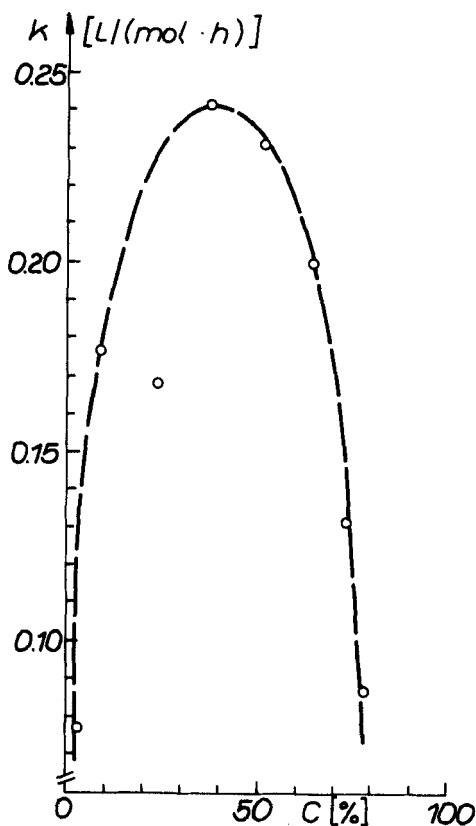


FIG. 2. Reaction of propene-MAN copolymers with aniline in DMF. 298 K. $C_{0,A\text{hydride}} = C_{0,A\text{mine}} = 0.1$ mol/L.

that the ethene-MAN and propene-MAN copolymers contain, respectively, 15 and 20% *erythro* configuration. Since they were determined by extrapolation to zero conversion, the k values of the copolymers so obtained are attributed to the "faster" *erythro* configuration. The polymer-specific influence can be eliminated almost entirely by using this extrapolation method for the MAN copolymers. The k values for the portion of the *erythro* configurations in the copolymer ought to represent, therefore, the reactivity of these functional groups in just about the right way. Comparison of the *erythro* configuration in the ethene-MAN copolymer with *erythro*-2,3-diethyl-SAN, having relative

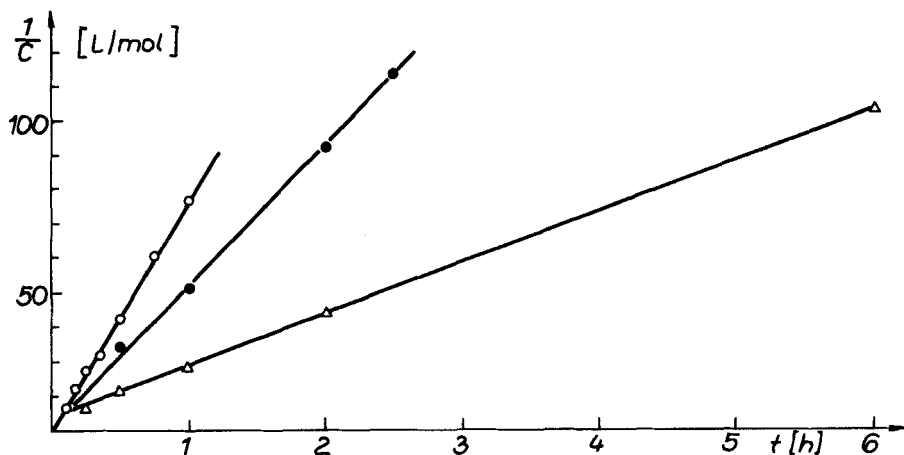


FIG. 3. Reaction of SAn (○), *erythro*- (●), and *threo*- (△) 2,3-diethyl-SAn with aniline in DMF/acetic acid 10/1 (v/v). 298 K. $C_{0,\text{Anhydride}} = C_{0,\text{Amine}} = 0.1$ mol/L.

k values of 0.58 and 0.62, confirms this statement. The rate constant obtained for the propene-MAN copolymer corresponds to the reactivity of an *erythro*-2-isopropyl-3-*n*-propyl-SAn. These observations are in accordance with the Flory concept of constant reactivity of the functional groups.

Reactions with Excess of Anhydride

An excess of anhydride groups was used to keep the variations in the polymer molecule caused by the generation of carbonyl and amide groups and the

TABLE 1. Reaction of Model Compounds with Aniline (equimolar)^a

	k , L/(mol·h)	Relative
SAn	66.6	1
<i>threo</i> -2,3-Diethyl-SAn	15.8	0.24
<i>erythro</i> -2,3-Diethyl-SAn	41.4	0.62

^aSolvent DMF; DMF/acetic acid 10/1 (v/v); $C_{0,\text{Amine}} = C_{0,\text{Anhydride}} = 0.1$ mol/L; $T = 25^\circ\text{C}$.

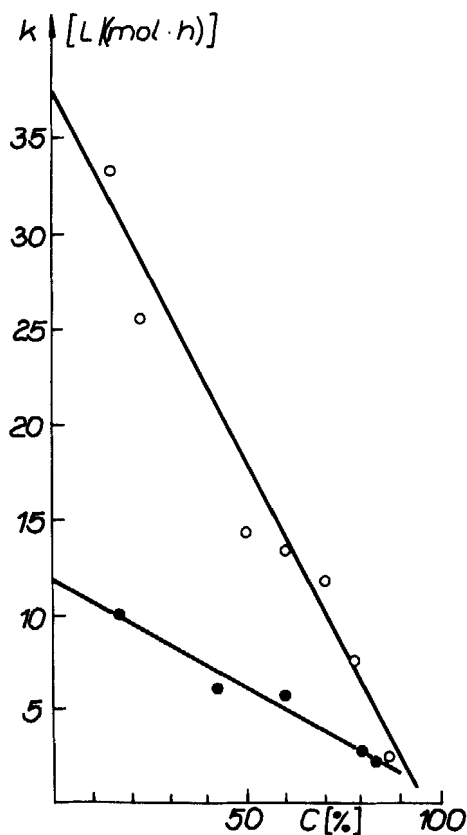


FIG. 4. Dependence of "rate constant" on conversion for the reaction of ethene- (○) and propene- (●) MAN copolymers with aniline in DMF/acetic acid 10/1 (v/v). $C_{0,\text{Anhydride}} = C_{0,\text{Amine}} = 0.1 \text{ mol/L}$.

TABLE 2. Reaction of Copolymers with Aniline (equimolar)^a

	$k, \text{ L}/(\text{mol}\cdot\text{h})$	Relative (SAn = 1)
Ethene-MAN copolymer	37.7	0.58
Propene-MAN copolymer	11.9	0.18

^aSolvent DMF; DMF/acetic acid 10/1 (v/v); $C_{0,\text{Amine}} = C_{0,\text{Anhydride}} = 0.1 \text{ mol/L}$; $T = 25^\circ\text{C}$.

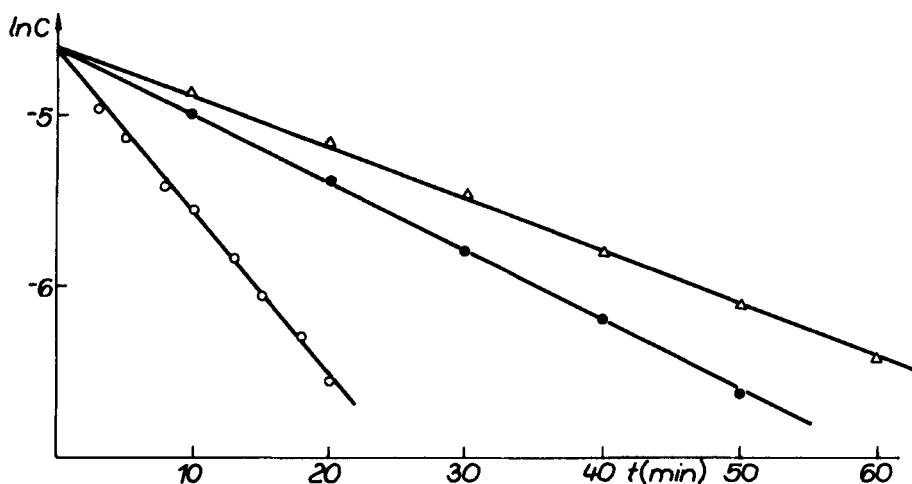


FIG. 5. Reaction of SAN (○), *erythro*- (●), and *threo*- (△) 2,3-diethyl-SAN with aniline in DMF/acetic acid 10/1 (v/v). 298 K. $C_{0,\text{Anhydride}} = 0.1 \text{ mol/L}$; $C_{0,\text{Amine}} = 0.01 \text{ mol/L}$.

related variation of the solution state as small as possible. By using this approach, we expected to be able to interpret the reaction of the copolymer and of the model compounds by using a pseudo-first-order rate law. The polymer-specific effect, which retards the reaction, should not be very noticeable for conversions up to 10% of the polymer molecule. To evaluate this concept, rate constants were determined for the model compounds (Fig. 5, Table 3).

The small difference between the relative k values of both configurations is striking. The ratio of the k values of the *erythro*/*threo* configuration decreases from 1/0.39 for the equimolar reaction to 1/0.6. The presence of “*erythro* impurity” in the *threo*-2,3-diethyl-SAN, which is preferentially produced because of the excess of anhydride, accounts for the differences.

Rate constants were determined for the MAN copolymers (Fig. 6, Table 4).

The k value of ethene-MAN copolymer lies, as expected, between the values for the *erythro* and *threo* configuration of 2,3-diethyl-SAN.

The k values of ethene- and propene-MAN copolymers are in the ratio 3/1, the same value already found for the equimolar amidation. Styrene-MAN copolymer has the lower reaction rate because of the greater steric influence of the benzene ring. The dependence of the molecular weight upon the rate

TABLE 3. Reaction of Model Compounds with Amine (tenfold excess)^a

	k, h^{-1}	Relative
SAn	6.0	1
<i>erythro</i> -2,3-Diethyl-SAn	3.0	0.5
<i>threo</i> -2,3-Diethyl-SAn	1.9	0.3

^aSolvent DMF; DMF/acetic acid 10/1 (v/v); $C_{0,\text{Anhydride}} = 0.1 \text{ mol/L}$; $C_{0,\text{Amine}} = 0.01 \text{ mol/L}$; $T = 25^\circ\text{C}$.

constants for the propene-MAN copolymers reflects the influence of the solution state of the polymers although only 10% of the anhydride groups on the polymer molecule are converted. The amidation reaction in solvent mixtures also shows polymer-specific effects. During the catalytic amidation of SAn with excess anhydride, the rate constants change proportionally to the mole ratio of the THF/DMF solvent. In contrast, a nonlinear dependence was found for the propene-MAN copolymer (Fig. 7).

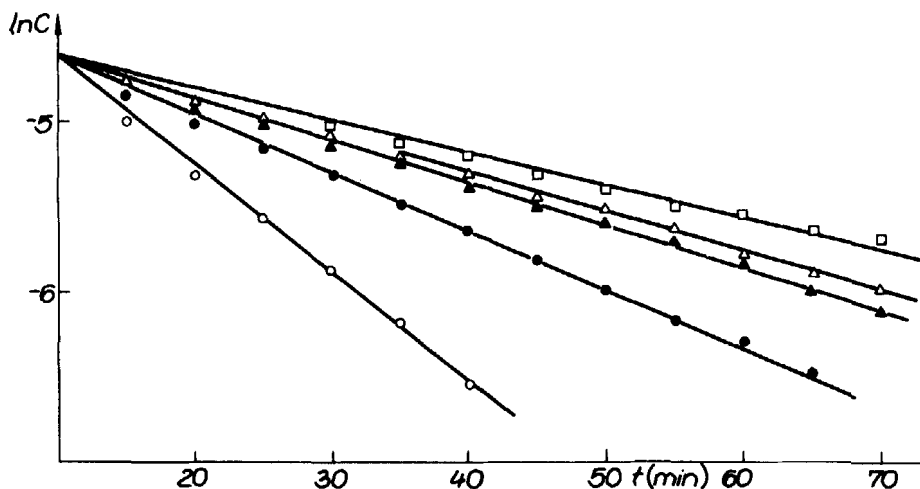


FIG. 6. Reaction of ethene- (\circ), propene- (\bullet , 11 000; \blacktriangle , 94 000; \triangle , 143 000 g/mol), and styrene- (\square) MAN copolymers with aniline in DMF/acetic acid 10/1 (v/v). 298 K. $C_{0,\text{Anhydride}} = 0.1 \text{ mol/L}$; $C_{0,\text{Amine}} = 0.01 \text{ mol/L}$.

TABLE 4. Reaction of Copolymers with Amine (tenfold excess)^a

	\bar{M}_n	k, h^{-1}	Relative (SAn = 1)
Ethene-MAN copolymer	6 000	2.5	0.41
Propene-MAN copolymer	11 000	0.98	0.165
	99 000	0.73	0.124
	143 000	0.69	0.115
Styrene-MAN copolymer	143 000	0.48	0.08

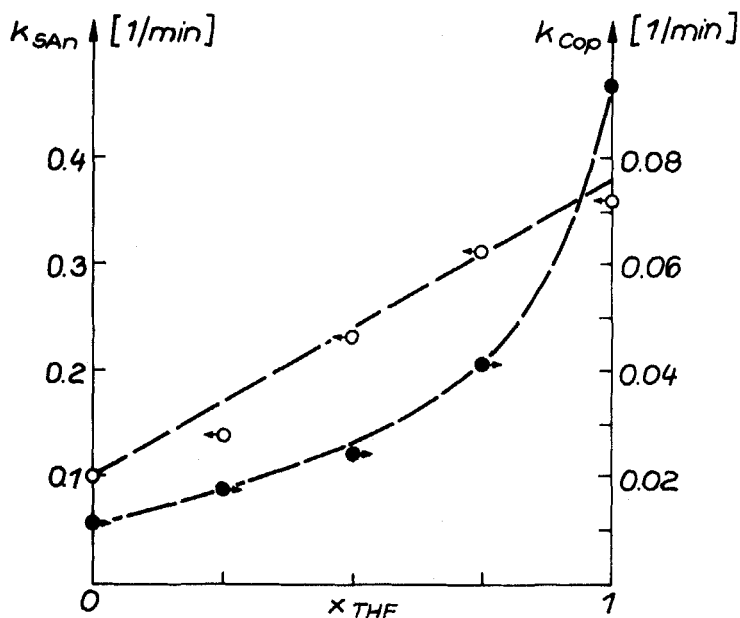
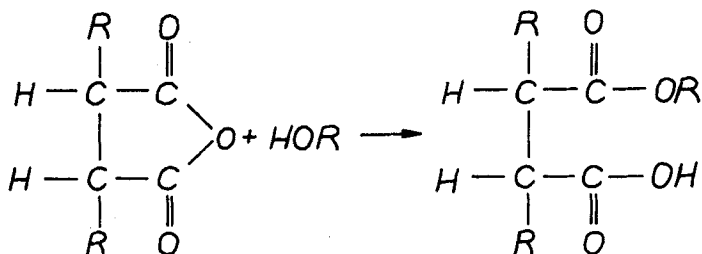
^aConditions: see Table 3.

FIG. 7. Reaction of SAn (○), and propene- (●) MAN copolymer with aniline in THF/DMF mixtures. Solvent mixture/acetic acid 10/1 (v/v). 298 K. $C_{0,A\text{nydride}} = 0.1 \text{ mol/L}$; $C_{0,A\text{mine}} = 0.01 \text{ mol/L}$.

A more than proportional increase of k with decreasing DMF content can be observed in the range of low DMF contents, whereas a smaller than proportional decrease of k with decreasing THF content is observed in the range of low THF contents. This behavior is due to a stronger DMF-MAN copolymer interaction, leading to specific solvation of the polymer molecule which affects the rate of reaction of the polymer molecule.

Esterification Reaction

Bouvier and Bruneau [6] obtained comparable rate constants for monoester formation with hexadecanol from *erythro*-2,3-diethyl-SAN and 2,3-dipropyl-SAN (preponderantly *erythro* configuration). Monoesters are formed during the reaction of the anhydrides with alcohol according to the following scheme:



As in the amidation reaction described above, a tenfold excess of anhydride was used. This made interpretation possible by a pseudo-first-order rate law. The results are shown in Table 5. The influence of the configuration of the anhydride on the rate constant is very noticeable. The *erythro* configuration reacts faster, as expected, although the differences are not as marked as in the case of amidation.

The differences between the rate constants of both copolymers are not considerable, while the dependence on the molecular weight is stronger than for the amidation, which can be attributed to polymer-specific effects, particularly because the polymers react more slowly than the model compounds. The small differences of the rate constants between the configurations and both polymers for esterification compared to amidation is caused by an absolute rate which is smaller by two orders of magnitude.

Hydrolysis Reaction

The ratios of the reactants corresponded to those of amidation and esterification, but the reaction rate was very low. In order to adapt the reaction

TABLE 5. Esterification Reactions (tenfold excess)^a

	\bar{M}_n	k, h^{-1}	Relative
SAn		0.069	1
<i>erythro</i> -2,3-Diethyl-SAn		0.035	0.50
<i>threo</i> -2,3-Diethyl-SAn		0.029	0.42
Ethane-MAn copolymer	5 000	0.026	0.37
Propene-MAn copolymer	11 000	0.028	0.40
	94 000	0.022	0.31
	143 000	0.017	0.25

^aSolvent DMF; $C_{\text{O, Anhydride}} = 0.1 \text{ mol/L}$; $C_{\text{O, Ethanol}} = 0.01 \text{ mol/L}$; $T = 60^\circ\text{C}$.

rate to the analytical procedure, triethylamine was used as a catalyst. In this case too, an interpretation was possible by using a pseudo-first-order rate law (Table 6).

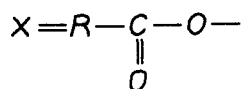
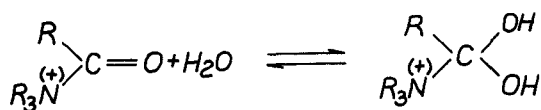
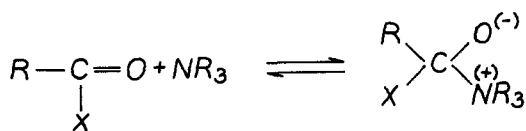
The constancy of the rate constant for the two configurations of the substituted SAn is remarkable. Since their different reactivities are attributed

TABLE 6. Hydrolysis Reactions (tenfold excess, catalyzed)^a

	\bar{M}_n	k, h^{-1}	Relative
SAn		0.210	1
<i>erythro</i> -2,3-Diethyl-SAn		0.115	0.5
<i>threo</i> -2,3-Diethyl-SAn		0.120	0.5
Ethene-MAn copolymer	5 000	0.024	0.12
	11 000	0.022	0.11
	94 000	0.018	0.09
	143 000	0.013	0.06

^aSolvent DMF; $C_{\text{Triethylamine}} = 0.2 \text{ mol/L}$; $C_{\text{O, Anhydride}} = 0.1 \text{ mol/L}$; $C_{\text{O, Water}} = 0.01 \text{ mol/L}$; $T = 65^\circ\text{C}$.

to differences in the ring strain and not to steric effects, the reason should be a reaction course different from that for amidation and esterification. We follow the Lowry and Richardson [13] concept, according to which direct attack of the catalyst in nucleophilic catalysis by tertiary amine occurs via a reactive intermediate. The rate-determining step has to be the subsequent reaction of the latter.



Then the rate-determining attack of the water takes place at the previous opened ring, and the influence of the different ring strains of both configurations is canceled out. The rate constants for the hydrolysis of the polymers differ strongly from those of the low-molecular weight model compounds. As already stated for esterification, practically no differences exist between ethene- and propene-MAn copolymers. The large difference of re-

activity between the low-molecular weight compounds and the polymer anhydrides is regarded as essentially due to the polymer-specific effect discussed above. Since triethylamine acts as a precipitant for MAN copolymers, the solution state of the polymer can be the reason for its low reaction rate. Indeed, the present investigations were performed with visually clear solutions, but further addition of amine results in precipitation of the polymer. This reasoning rests upon the strongly marked decrease of the rate constants with increasing molecular weight, even though conversion of the anhydride moieties amounted to at most 10%.

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