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Amidification of poly(styrene-co-maleic anhydride) with amines in tetrahydrofuran solution: A kinetic study

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SUMMARY

The kinetics of the reaction between a styrene-maleic anhydride copolymer (SMA) and amines was investigated in tetrahydrofuran solution between 0°C and 40°C. This reaction converts the maleic anhydride (MA) into the corresponding amide-acid, while the consecutive reaction of the generated acid with amine forming a diamide or transformation of the acid-amide into the imide was not observed. The amine reactivity follows the order: 1-octylamine $>>$ 1-methyl hexylamine $>>$ 1,1-dimethyl propylamine or dibutylamine, demonstrating that the amine reactivity depends, to a large extent, upon its steric hindrance. This reaction is reversible as shown by IR at high temperatures, but the reverse reaction was undetectable between 0 and 40°C. The overall reaction involves spontaneous and autocatalytic reactions, and the overall reaction rate can be written as: $-d[MA]/dt = k_0[MA][-NH_2] + k_1[MA][-NH_2]^2$. In the case of 1-octylamine below 0.02 M, the spontaneous reaction dominates (i.e, $k_0 >> k_1[-NH_2]$).

INTRODUCTION

The reaction between anhydride and amine is well-known in organic chemistry. It has also gained numerous applications in polymers in general[1,2,3], and in the field of reactive extrusion in particular[4,5,6,7,8]. To the authors' knowledge, however, no detailed kinetic data for this type of reaction has been reported neither in polymer nor in organic chemistry literature. The primary reason would be that this type of reaction generally proceeds too fast to allow collection of kinetic data; and probably because of the fast reaction rates, there has been no real interest in its kinetics in detail as long as the chemistry works in a given application .

We have been interested in devolatilization of reactive polymer solutions[9] using a screw extruder, where a quantitative description of the reaction path is crucial. This paper presents the mechanistic and kinetic aspects of the reaction between polystyrene supported maleic anhydride residues and amines, chosen as a model reaction for the devolatilization study.

EXPERIMENT

Materials: The polymer used as a reactant substrate was a commercial (ARCO chemical company) grade of poly(styrene-co-maleic anhydride) (SMA) with 8.0 wt% of the MA. Its number and weight mass molecular weights were 120,000 g/mole and 270,000 g/mole, respectively. The amines (1-octylamine, 1-methyl hexylamine, 1,1-dimethyl propylamine and dibutylamine) were purchased from Aldrich and used as received. The solvent, tetrahydrofuran (anhydrous, 99.9%, denoted as THF), was also purchased from Aldrich. It was stored with sodium and distilled before use.

Reactor: A standard three neck flask (250 cm^3) was used as the reactor, which was agitated

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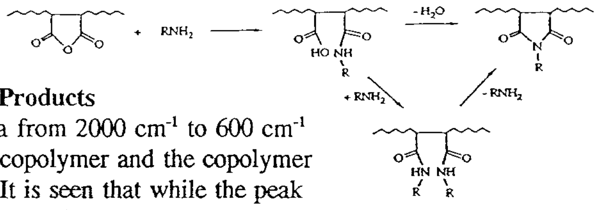
with a simple blade rotating at 100 rpm. Above the room temperature, the temperature was controlled within ± 0.2°C by a silicon oil bath which was attached to a precision temperature control unit. The temperature 0°C was obtained an ice-water mixture.

Analysis: Reaction solution samples were collected at regular time intervals. They were precipitated in hexane, filtered, dissolved in THF, precipitated again, filtered, and then redissolved in THF. The purified solutions were then deposited on a NaCl window and dried up for IR analysis. The conversion was followed by choosing the out-of-plan ring bending peak at 701 cm^{-1} associated with the phenyl group of SMA as the internal reference and the one at 1780 cm^{-1} assigned to the MA residues as the target.

RESULTS AND DISCUSSION

Several consecutive reactions between an anhydride and a primary amine can occur, depending primarily upon the reaction temperature[3]:



IR Characterization of the Reaction Products

Fig.1 compares the infrared spectra from 2000 cm^{-1} to 600 cm^{-1} of the virgin styrene-maleic anhydride copolymer and the copolymer completely reacted with 1-octylamine. It is seen that while the peak at 701 cm^{-1} characteristic of the out-of-plan ring bending of the phenyl group of the SMA does not vary with the reaction, the ones at 1855 cm^{-1} and 1780 cm^{-1} assigned to the MA residues are absent from the polymer product, indicating that the reaction has been complete. Additionally, two new peaks appear at 1654 cm^{-1} and 1556 cm^{-1}, corresponding to the amide generated. The broad nature of these two peaks would result from the complexation between the coupled amide and the carboxyl residue. This is supported by a new weak peak at 1390 cm^{-1}, corresponding to the COO$^-$ symmetric vibration[4]. A very broad peak at 1731 cm^{-1} is also noted after the reaction, which may be attributable to the carboxyl residues. Although the

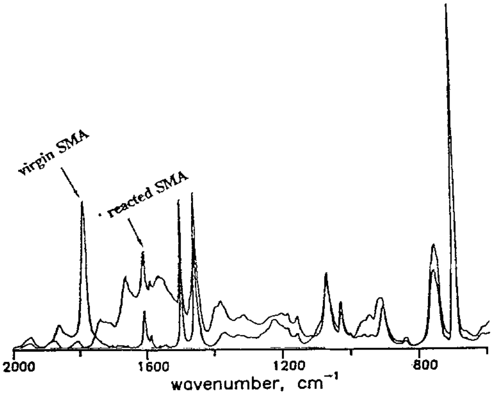


Fig.1 IR spectra of the SMA copolymer before and after reaction

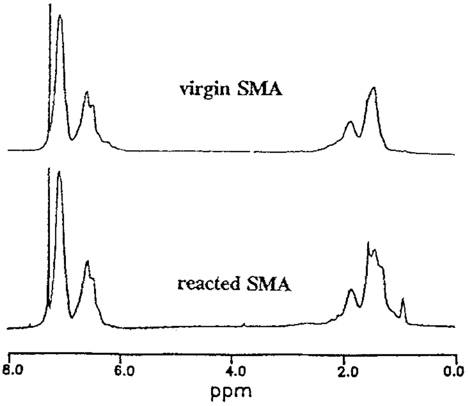


Fig.2 H^1 NMR spectra of the SMA copolymer before and after reaction

IR spectra shown in Fig.1 can not exclude the formation of the diamide, they seem to suggest that no imide (which would bring about a peak at 1700 cm^{-1}) is formed. Fig.2 shows the H^1 NMR spectra of the SMA before and after reaction with 1-octylamine. It is noted that after the reaction, the original peak at 1.4 ppm is split into three overlapping peaks. Additionally, a new peak appears at 0.9 ppm, which is attributable to the protons of the methyl group of the amine grafted onto the MA residues. However the H^1 NMR also fails to provide information about whether the diamide or imide is formed.

Fig.3 is the difference spectrum of the two shown in Fig.1. The downturn of the peaks at 1855 cm^{-1} and 1780 cm^{-1} indicates that the MA residues have been consumed, while the broad peak between 1740 cm^{-1} and 1495 cm^{-1} stems from the generated species.

If IA denotes the integral area of the absorbance vs. wavenumber of the difference spectrum between 1740 cm^{-1} and 1495 cm^{-1} (cf: Fig.3), $R = A_{1780}/A_{701}$ (A_{1780} and A_{701} represent the absorbance of the peak at 1780 cm^{-1} and that at 701 cm^{-1}, respectively), then $IA/IA_{100\%}$ and $R/R_{0\%}$, both representing the extent of reaction, should be equal if the acid-amide is the only reaction product ($IA_{100\%}$ is the IA value when the maleic anhydride is entirely reacted; $R_{0\%}$ is the R value when no reaction occurs). Fig.4 shows that $IA/IA_{100\%}$ matches fairly the respective $R/R_{0\%}$, implying that the further reactions mentioned above, forming the imide and/or diamide, are unimportant if not nonexistent at all at the low reaction temperatures. This finding is also consistent with the fact that the transformation of the acid-amide into the imide or diamide proceeds much more slowly than the formation of the acid-amide from anhydride and amine[3]

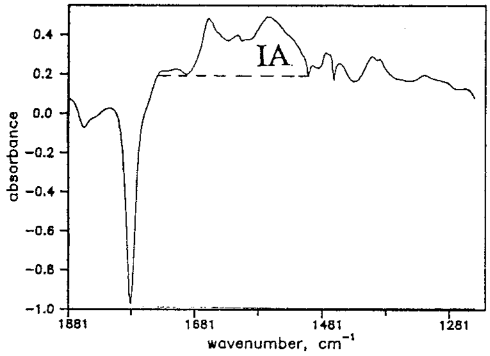


Fig.3 Difference IR spectrum of the SMA before and after reaction

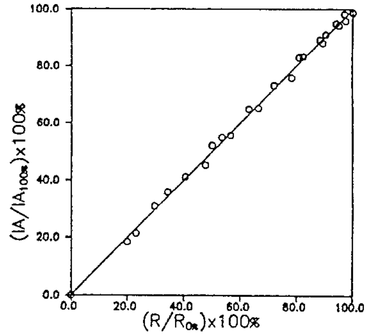


Fig.4 Graphical representation of $IA/IA_{100\%}$ vs. $R/R_{0\%}$

Reversibility of The Reaction

The reversibility of the reaction has never been mentioned in the literature. It was examined in this study as follows: after being completely reacted with 1-octylamine at the room temperature, the SMA copolymer was dissolved in THF, and a thin film was then made out of it on a NaCl window. After its IR spectrum was recorded, it was placed in a vacuum oven at 140°C for 12 hours, and the IR spectrum of the treated sample was recorded. Fig.5 shows that after such a thermal treatment, while the peaks which represent the acid-amide disappeared completely, a new peak at 1700 cm^{-1} indicating the formation of the imide appeared. More importantly, it is seen that most of the reacted maleic anhydride residues was also recovered (cf: the reappearance of the peaks at 1780 cm^{-1} and 1855 cm^{-1}), meaning that the acid-amide also went back to the MA during the thermal treatment. It is therefore concluded that the reaction between anhydride and amine forming the corresponding acid-amide is reversible, similar to the reaction between anhydride and alcohol generating the corresponding acid-ester[10]. But in the temperature range within which the kinetic study was performed, the reverse reaction is unimportant as the final conversions always reached their limits possible at 0.0°C and 40.0°C (cf: Fig.6)

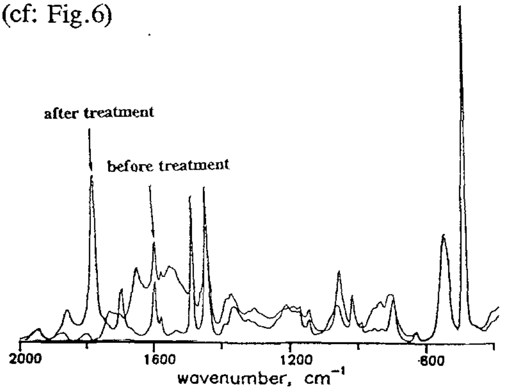


Fig.5 IR spectra of a completely reacted SMA sample before and after thermal treatment

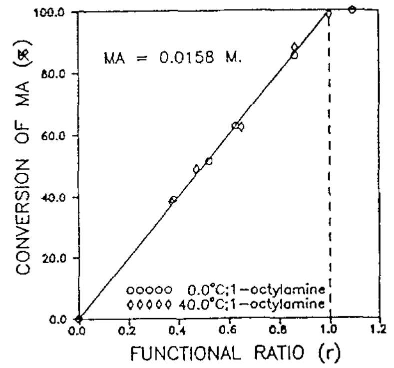


Fig.6 Maximum conversion vs. functional ratio

Reactivity of the Amines

The reactivity of several amines attached to different alkyl substituents was examined and shown in Fig.7. It is noted that 1-octylamine is much more reactive than 1-methyl hexylamine. On the other hand, 1,1-dimethyl propylamine and dibutylamine do not show any detectable reactivity. This clearly demonstrates that the steric hindrance affects greatly the amine reactivity. Below, 1-octylamine is used for the present kinetic studies.

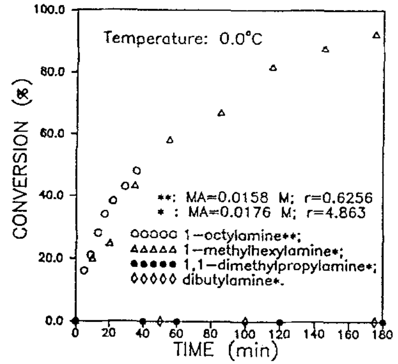


Fig.7 Reactivity of amines of different alkyl substituents

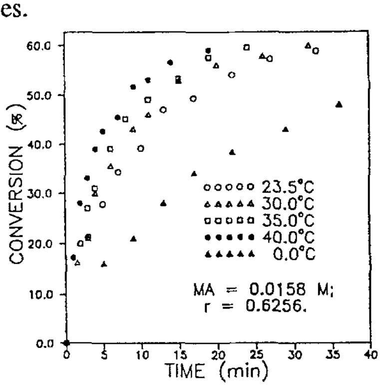
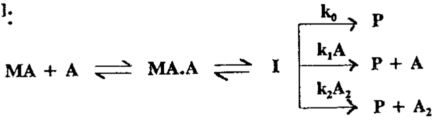


Fig.8 Conversion vs. time of SMA/1-octylamine system

Kinetics of SMA/1-Octylamine System

To the authors' knowledge, the mechanism of the reaction between anhydride and amine has not been directly addressed in the literature. It is plausible that it is similar to that of the aminolysis of an ester[11]:



The amine molecule (A) attacks the maleic anhydride substrate (MA) forming a molecular complex (MA.A). The latter then undergoes a chemical change to yield the tetrahedral intermediate (I) which can decompose into the final product P. The decomposition of I into P is believed to be the rate controlling step, and it may be spontaneous (k_0) or may be catalyzed by an amine monomer (k1) or by an amine dimer (k_2). According to this mechanism together with the experimental fact that the reverse reaction is unimportant at the low temperatures, the overall reaction rate can then be written as

$$-\frac{d[MA]}{dt}=k_0[MA][-NH_2]+k_1[MA][-NH_2]^2+k_2[MA][-NH_2]^3+\ldots \qquad (1)$$

where the first term of the right side corresponds to the spontaneous reaction, the second and the remaining terms result from the autocatalytic effect of the amine itself.

If a and b denote the initial molar concentrations of the MA and the amine, r is defined as b/a, and assuming that only the first two terms are responsible for the overall reaction rate, then

$$\frac{dp}{dt} = k_0 a(1-p)(r-p) + k_1 a^2(1-p)(r-p)^2 \qquad (2)$$

It is useful to introduce the relative importance of the autocatalytic reaction over the spontaneous one by defining a ratio R:

$$R = \frac{k_1 a^2(1-p)(r-p)^2}{k_0 a(1-p)(r-p)} = \frac{k_1 a(r-p)}{k_0} = \frac{k_1}{k_0}[-NH_2] \qquad (3)$$

It is seen that R is proportional not only to the ratio k_1/k_0, characteristic of a particular reacting system, but also to the amine concentration which is a parameter of the experiment.

Integration of Eq.1 yields:

$$S_{01} = \frac{1}{a(r-1)k_0}\ln\frac{r-p}{r} - \frac{1}{a(r-1)[k_0+a(r-1)k_1]}\ln(1-p)$$

$$-\frac{k_1}{k_0^2+a(r-1)k_0k_1}\ln\frac{k_0+ak_1(r-p)}{k_0+ak_1 r} = t \qquad (4)$$

When either the spontaneous or autocatalytic reaction dominates, Eq.4 reduces to

$$S_0 = \frac{1}{a(r-1)}\ln\frac{1-\frac{p}{r}}{1-p} = k_0 t \quad (\textit{spontaneous, } R < 1) \tag{5}$$

$$S_1 = \frac{1}{[a(r-1)]^2}\left[\ln\frac{1-\frac{p}{r}}{1-p} - \frac{p(r-1)}{r(r-p)}\right] = k_1 t \quad (\textit{autocalytic, } R > 1) \tag{6}$$

Since the reaction of the maleic anhydride with 1-octylamine is very fast, it had to be conducted in dilute solutions (about 2 to 3 w.t.% copolymer) at low temperatures (< 40°C). Fig.8 shows the conversion as a function of time under various temperatures. As expected, the reaction rate increases with increasing temperature. However, the magnitude of the rate increase is not very significant. Since the rate constants k_0 and k_1 in Eq.4 can not be obtained without going through an optimization process, Eqs.5 and 6 were first tested against the experimental data in Fig.8. It was found that only Eq.5 fits the data satisfactorily well (cf: Figs.9 and 10). This is also supported by the fact that utilization of Eq.4 yielded k_0 values which were very close to those obtained from Fig.9, while k_1 values were almost zero. This indicates that under the present experimental conditions (particularly the amine concentration was very small), the autocatalytic reaction is negligible, if not nonexistent at all. Unfortunately, a quantitative evaluation of the autocatalytic reaction for this amine was not possible even at the lowest temperature (0.0°C), because the reaction was too fast to further increase the amine concentration in order to make the autocatalytic reaction (k_1) detectable.

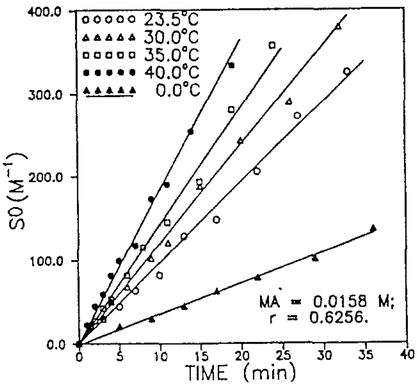


Fig.9 Fit of Eq.5 to the data in Fig.8

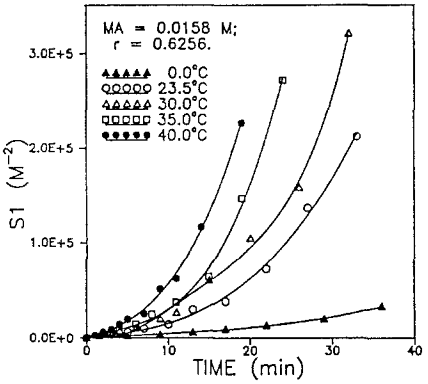


Fig.10 Fit of Eq.6 to the data in Fig.8

The effect of the amine concentration (within a limited range) on the overall reaction rate is shown in Fig.11. Eqs.5 and 6 were used to fit the data in this figure. Here again, Eq.5 gave a single straight line (cf: Fig.12), whereas Eq.6 yielded separate curves. This confirms that the spontaneous reaction does dominate under the reaction conditions. The temperature dependence of k_0 can be expressed by

$$k_0 = 7.25x10^5 \, e^{-\frac{3332}{T}} \quad (M^{-1}\mathrm{min}^{-1})$$

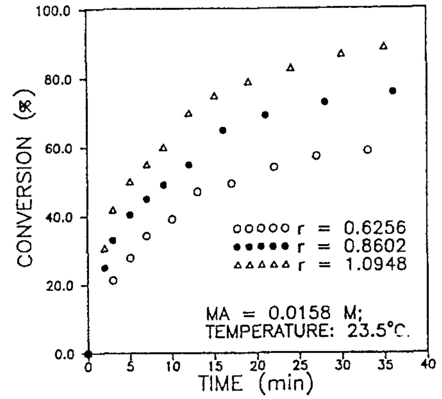


Fig.11 Conversions at various amine concentrations

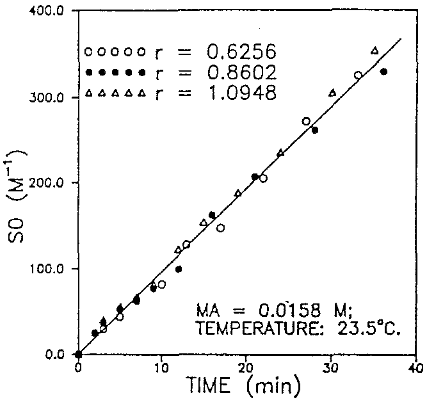


Fig.12 Fit of Eq.5 to the data in Fig.11

CONCLUDING REMARKS

In this paper, the reaction of the maleic anhydride residues in a styrene-maleic anhydride copolymer with 1-octylamine, forming the corresponding acid-amide, has been investigated between 0°C and 40°C. While the overall reaction is reversible as demonstrated by the IR technique, the reverse reaction has not been detected in the reaction temperature range investigated. The reactivity of amines follows the order: 1-octylamine > > 1-methyl hexylamine > > 1,1-dimethyl propylamine or dibutylamine, implying that steric hindrance of the amine is primarily responsible for its overall reactivity. Because the high reactivity of 1-octylamine, the reaction had to be conducted in dilute solutions. It has been shown that when the amine concentration is below 0.02 M, the spontaneous reaction dominates and the rate can be described as: $-d[MA]/dt = k_0[MA][-NH_2]$.

REFERENCES:

1. B.C.Trivedi and B.M.Culbertson, "Maleic Anhydride", Plenum Press, New York (1982)
2. D.Tsiourvas, C.M.Paleos and P.Dais, J.Polym.Sci., Chem.Ed., Vol.28, 1263 (1990)
3. Martine Tessier and Ernest Marechal, J.Polym.Sci., Chem.Ed., Vol.26, 2785 (1988)
4. C.E.Scott and C.W.Macosko, Polym.Preprints, Vol.29, No.1, 561 (1988)
5. B.K.Kim and S.J.Park, J.Appl.Polym.Sci., Vol.43, 357 (1991)
6. A.Nicco, J.Hubert, J.Druz and M.Lambla, US pat. 4,612,349 (Sept.16,1986)
7. M.Lambla, A.Killis and H.Magnin, Eur.Polym.J., Vol.15, 489 (1979)
8. S.Cimmino, F.Coppola, L.D'Orazio, R.Greco, G.Maglio, M.Malinconio, C.Mancarella, E.Martuscelli and G.Ragosta, Polymer, Vol.27, 1874 (1986)
9. L.Q.Chen, G.H.Hu and J.T.Lindt, accepted by AIChE J.
10. G.H.Hu and J.T.Lindt, accepted by J.Polym.Sci.
11. O.B.Nagy, V.Reuliaux, N.Bertrand, A.V.D.Mensbrugghe, J.Leseul and J.B.Nagy, Bull.Soc.Chim.Belg., Vol., (1985), and references therein.

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