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## ABSTRACT

*The kinetics of graft copolymerization of maleic anhydride to tetradecene in 1,2 – dichlorobenzene has been investigated. At high initiator concentration, the rate of disappearance of maleic anhydride is linear with time and the order with respect to initiator is close to 0.5 while the average number of maleic anhydride molecules grafted per molecule of initiator decomposed varies from 8 at high rates of initiation to 57 at low rates of initiation. The results are interpreted in terms of a chain mechanism including a propagation step in which a succinic acid molecule abstracts hydrogen from the hydrocarbon chain.*

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## INTRODUCTION

Interest in graft copolymerization arises in part from the protection conferred by the grafts on the polymer backbone and this specific feature has led to applications such as emulsifiers, surface modifying agents, coating materials and compatibilizers in polymer blends<sup>1-3</sup>. Maleic anhydride, for example, is an interesting building block in grafting reactions to compounds such as olefins, cycloalkenes, dienes<sup>4</sup> etc. Newly developed products such as bismaleimides<sup>5</sup> using maleic anhydride are of growing importance as high performance materials especially for composites with carbon and high modulus fibres. Owing to the importance of the anhydride reactions, a lot of literature has been generated on kinetics such as those with acrylamide<sup>6</sup>,

ethylacetate, acrylonitrile<sup>7</sup>. Investigations on the copolymerization of maleic anhydride with 2,4,4- trimethylpent -2-ene<sup>8</sup> and comparisons of ethenyl with other alkenes demonstrate that the copolymerization rate is dependent on co-olefin  $e$ -value, the solvent and steric hinderance during anhydride addition to the radical chain end of the co-olefin. Other studies include the influence of solvent and the total polymerization rate in the copolymerization of maleic anhydride with cyclopentene, norbornene and dicyclopentadiene<sup>9</sup>. The dependence of total polymerization rate of monomer pair, cyclopentadiene / maleic anhydride, on the donacity of the solvent shows a linear decrease while those of maleic anhydride with 1, 4- hexadiene, norbornene yield a

copolymer with maleic anhydride content greater than 50mol% in dioxane<sup>10</sup>. Keller et al<sup>11</sup>. Carried out investigation which was later reviewed in detail by Hill et al<sup>12</sup>. Fujimuri et al<sup>13</sup>. Have also carried out a detailed measurement study on the same system and a complex participation model proposed by Geogiere and Zubov<sup>14</sup> proved very satisfactorily. Interesting compounds that can be obtained if maleic anhydride is grafted to alkenes such as conjugated and non - conjugated dienes include products with improved adhesion properties and enhanced ability to form polymer blends<sup>1-3</sup>. Conjugated dienes tend to form 1:1 Diels Alder adducts instead of copolymerizing while non - conjugated dienes can react to form 1:1 or 1:2 copolymers with vinyl groups which are cyclic<sup>15</sup>. A more extensive description of the current knowledge on the kinetics of copolymerization of maleic anhydride with dienes is found in Ratzch<sup>16</sup>. In his report on the reaction of maleic anhydride with hexadienes using dioxane as a solvent and dibenzyl peroxide as initiator, copolymers without free double bonds and of norbornene were obtained. In all, the anhydride content increases to more than 50mole% with rise in initiator concentration. More studies have also been performed with aromatic monoamines<sup>17</sup> where interpretation was performed by a second order rate law and the average measured data were available up to 65%. Other measurements from ethyl - maleic anhydride copolymers, in the presence of glacial acetic<sup>18</sup>, show a rate decrease which is larger than would be consistent with a second order rate law. In this paper, we are presenting our investigation of the grafting of maleic anhydride to the hydrocarbon tetradecene.

## EXPERIMENTAL

### *Materials*

All reagents used in this work were Analar grade obtained from ICI (UK). Tetradecene and 2,-dimethyl-2,5-di(t-butylperoxy) - 3 - hexyne were supplied with the assistance of Dr. P. Fawcett, Chemistry Department, Queen's University of Belfast, N. Ireland. The ir spectrometer was a Pye Unicam (Model SP 1004DB) while the nmr spectrometer was a Bruker FT 400.

### *Synthesis*

Maleic anhydride was grafted to tetradecene by the method of Gaylord<sup>19</sup> but initiated with 2,5-dimethyl-2,5-di(t-butylperoxy) - 3 - hexyne in 1, 2 - dichlorobenzene. The product (8.10g) was separated in methylene chloride - hexane mixtures, dried in vacuo at 60°C and analyzed by ir using a KBr disc and nmr where samples were dissolved in acetone-d<sub>6</sub> and shifts referenced to tetramethylsilane.

### *Kinetic Measurements.*

The rates of disappearance of maleic anhydride was determined from homogenous solution of tetradecene in 1, 2 - dichlorobenzene at 140 - 180°C with 2,5-dimethyl-2, 5-di (t-butylperoxy) -3-hexyne (0.001M - 0.05M) initiator. Samples (0.50ml) were removed at intervals, dissolved in dry toluene (5.0ml) and absorbance measured at 300nm on a 397 Pye Unicam UV-Visible Spectrometer to obtain the amount of anhydride remaining in the reaction mixture. The results were then converted to rates of disappearance using a calibration data obtained in separate experiments.

## RESULTS AND DISCUSSION

Ir data of fractions show a strong band at 1786cm<sup>-1</sup> and a weaker band at 1863cm<sup>-1</sup> suggesting the presence of succinic anhydride group on the hydrocarbon chain.

The spectrum of the remaining hydrocarbon solution showed that the rest of the anhydride had been converted to soluble products which also contain the succinic anhydride group. This is probably the grafted material since non-grafted products such as succinic anhydride, which are almost insoluble in hydrocarbon if formed, would have shown up in the spectrum. Greater structural details in the proton spectrum show a complex multiplet

in the 2.8 - 3.4ppm region and other peaks at 3.0, 3.1 and 3.4ppm close to that observed for dodecyl succinic anhydride<sup>20</sup>. The multiplet is therefore, by analogy, assigned to three protons of the succinic anhydride group; the absence of peaks at 4.0 - 5.0ppm in the <sup>1</sup>H nmr, where poly-maleic anhydride normally shows a broad group of resonances further proves that the anhydride rings are not in form of chains.

Table 1: Data for the rate of grafting maleic anhydride to tetradecene.

Temp °C	Initiator Conc x 10 <sup>3</sup> M	-dMA x 10 <sup>-5</sup> dt MS <sup>-1</sup>	Grafting yield (%)
140	1.0	0.34	57
140	5.0	0.81	27
140	10.0	1.26	21
140	20.0	1.62	14
140	50.0	2.88	10
150	1.0	0.90	56
150	5.0	1.89	23
150	10.0	2.79	17
150	20.0	3.87	12
150	50.0	7.20	8.4
160	1.0	1.52	26
160	5.0	3.58	12
160	10.0	4.96	8.5
170	1.0	2.97	17
170	5.0	7.74	8.9
180	10.0	5.0	11.0

### Kinetic Measurements

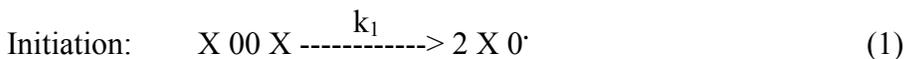
When data for a high initiator concentration (0.02M) at 150°C is examined the curve in Fig. 1 was obtained. There is little sign of an induction period and the rate of loss of maleic anhydride is almost independent of time over the first 60% reaction. The rate decreases during the later stages and small absorbance is observed at the end of the reaction. In this experiment, the concentration of initiator

decreases to 0.018M during the first 60% of reaction i.e. it is almost constant, and the linear section of Fig. 1 indicates that order with respect to maleic anhydride is close to zero. During the later stages of the reaction, when the maleic anhydride concentration has dropped to about 0.01M, the rate falls implying that the order with respect to maleic anhydride is now greater than zero. At low initiator concentrations, e.g. 0.001M, the maximum rate of reaction

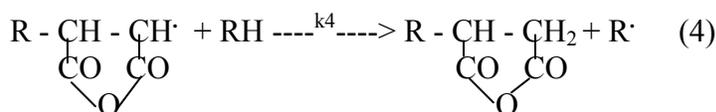
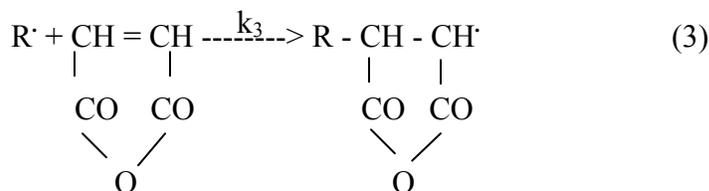
is observed when approximately 10% of maleic anhydride has disappeared and it decreases slowly but continuously as the reaction proceeds. When the disappearance of maleic anhydride from the reaction mixture (Table 1) was investigated, the order of reaction with respect to initiator was estimated to be 0.53 while the order with respect to anhydride is close to zero within individual experiments with an initial anhydride concentration of 0.025M. When decomposition of initiator is again measured at 140 - 170°C, the rate constants were found to be  $6.3 \times 10^{-5}$ ,  $1.7 \times 10^{-4}$ ,  $5.8 \times 10^{-4}$ , and  $1.7 \times 10^{-3}$  s respectively.

The reaction of maleic anhydride with tetradecene in the presence of a peroxy compound that decomposes at a measurable rate in the temperature range, 140 - 180°C, giving alkoxy radicals which readily abstract hydrogen atoms, produced grafts consisting of succinic anhydride groups. Since the poly - maleic anhydride chains are not formed as the monomer is above its ceiling temperature for polymerization at concentration 0.05M and temperature 140 - 170°C and the yield of succinic anhydride grafts per molecule of initiator decomposed is high (8-57), then it is suggested that the grafting reaction is occurring by a chain mechanism shown below:

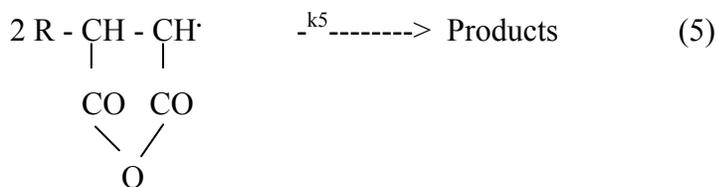
### Mechanism



Propagation:



Termination:



Where  $\text{X O O X}$  - Peroxy initiator  
 $\text{RH}$  - Alkene

In the above mechanism, the overall rate of disappearance of maleic anhydride is given as

$$\text{Rate} = k[\text{Initiator}]^{1/2} [\text{RH}] \quad -(6)$$

and Where  $k = k_4 [f k_1 / k_5]^{1/2}$   $f$  = number of radicals per initiator molecule which abstract hydrogen from tetradecene.

Table 2: Estimate of the number of grafts per tetradecene molecule.

Tetradecene samples	%Number of grafts on		Number of grafts determined from <sup>1</sup> H nmr
	Carbon	Hydrogen	
1	3.5	3.3	3.3
2	4.4	4.0	4.1
3	6.1	4.7	5.0

The observed order with respect to initiator is close to 0.5 and the order with respect to maleic anhydride is zero, in keeping with the above reaction scheme. The rate of reaction increases with concentration in 1,2 - dichlorobenzene solution when [RH] is below 100g/litre but it becomes independent of [RH] at higher concentration. The low order of reaction with respect to [RH] at concentrations greater than 100g/litre can be understood if chain propagation occurs intramolecularly rather than as intermolecularly. Estimates on number of grafts per tetradecene molecule using <sup>1</sup>H nmr (Table2) shows that about 2/3 of the maleic anhydride forms adduct containing 3-5 succinic anhydride groups per molecule. If a random distribution of succinic anhydride groups had occurred, the chance of there being more than one graft per any one molecule would have been very small. Thus intramolecular grafting is much preferred to intermolecular reaction. The greater dependence on [RH] at low hydrocarbon concentration can be explained by a reduced rate of initiation, and the fact that the fraction of initiator radicals which abstract hydrogen from the

hydrocarbon in equation 2 drops as the hydrocarbon concentration is decreased.

The graft yield in Table 1 indicates well the ratio of anhydride to initiator lost since anhydride loss can be changed by raising initiator concentration or temperature. As the rate of grafting is proportional to the square root of initiator concentration, then the rate of initiation (R<sub>i</sub>) is assumed proportional to concentration of initiator ([i]) and the graft yield approximately equal to reciprocal of square root of rates of initiation ([R<sub>i</sub>]<sup>1/2</sup>). The observations that the grafting rate increases with [i]<sup>1/2</sup> confirm that radicals disappear in pairs. The termination reaction (equation 5) is therefore written by analogy with the termination of peroxy radicals in autoxidation described by Howard's<sup>21</sup>. In that process, the Howard addition of oxygen is fast and at high enough oxygen concentrations, the rate - determining propagating step involves abstraction of hydrogen from the hydrocarbon by a peroxy radical.

### CONCLUSION

On the basis of results so far obtained, we conclude that the rate of grafting maleic

anhydride to tetradecene is proportional to the square root or initiator concentration but almost independent of anhydride concentration. Furthermore, under the conditions employed, a chain mechanism comparable to that accepted for autoxidation appears to be operative.

#### ACKNOWLEDGEMENT

We acknowledge the support of Dr. P. Fawcett of Chemistry Department Queen's University of Belfast for the Ir and <sup>1</sup>H nmr data on samples.

#### REFERENCES

1. Porejko, S., Gabra, W. and Kulesza, J., J. Polym. Sci. A - 1, 5 (1967) 1563.
2. Andrews, L. J. and Kefer, R.M., J. Am. Chem. Soc. 75 (1953) 3776.
3. Kazuhiko, M., Oniku, K. and Hiromichi, A., Eur. Pat App. Ep. 221 (1985) 576.
4. Shigeni, K. and Eichi, T., Kokai Tokkyo koho Jp. 62:147(1987) 510.
5. Chi, D. and Thomas, J.K., Polym. Mater. Sci. Eng. 57 (1987) 704.
6. Yoshimasi, K. and Ishinza, N., Kokai Tokkyo Koho Jp. 62: 152 (1987) 752. 10
7. Yoshiki, Y., Kokai, Tokk Jp. 62: 420 (1988) 873.
8. Arnold, M. and Steiner, V., Aca. Poly. 36 (1985) 8.
9. Gaylord, N. G. and Mahta, R., J. Polym. Sci. Poly. Lett. Ed. 20 (1982) 481.
10. Keller, F., Matzch, M. and Schneider, H., Plastic Kalltsch. 21 (1974) 262.
11. Hill, J. J. T., Odonnell, j. H O. and Sullivan, P.W., Macromolecules. 9 (1985) 18.
12. Fujimori, A. S., Stuart, A. and Craven, I. E., Makromol. Chem. 188 (1987) 2177.
13. Georgiere, G. S. and Zubov, V.P., Eur. Polym. J. 14 (1973) 93.
14. Yordankaza, I. J., Stotzkaya, U., Krezel, B. A., Ignatykaid, U. U. and Odinkov, V. N., Vysokomolk. Soedin. 8 (1978) 865.
15. Ratzch, M., J. Macromoloe. Sci. Chem. A24 (1990) 51.
16. Ratzch, M. and Reichter, G., Faserforsch. Txt. Tech. Z. Ponyefech. 29 (1993) 532.
17. Lionel, G. and Markus, H., PCT. Int. App. W. O. 86 (1994) 06394.
18. Gaylord, N. S., US Pat. 4: 506 (1985) 156.
19. Tanaka, H. and Kareko, Kokai. Tokkyo Koho Jp. 61:213 (1990) 245.
20. Howard, J. A., Adv. Free Radical Chem. 4 (1972) 49

*accepted 17/7/2003*

*received 28/11/2002*