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Corneliu Cincu[a]; Ferroudja Chatzopoulos[a]; Jean-Pierre Monthéard[a]
[a] Faculty of Sciences and Techniques, University of Saint-Etienne, FRANCE

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ALTERNATING COPOLYMERS: MALEIC ANHYDRIDE WITH CYCLIC OLEFINS. INFLUENCE OF THE CYCLIC OLEFIN ON THE COPOLYMERIZATION PROCESS AND PROPERTIES OF THE COPOLYMERS

Corneliu Cincu, Ferroudja Chatzopoulos and Jean-Pierre Monthéard*
Faculty of Sciences and Techniques, University of Saint-Etienne
Saint-Etienne Cedex 2 - FRANCE.

ABSTRACT

Maleic anhydride has been copolymerized with various cyclic olefins such as cyclohexene, cyclooctene, cyclododecene, norbornene, indene and thiophene. The resulting copolymers are alternating and the mechanism of the reaction can be explained by a charge-transfer complex. The influence of the starting cyclic olefin has been studied, and showing that the rate of the reaction largely depends on the nature of the olefin.

INTRODUCTION

It is well known that certain free radical copolymerization systems containing electron donating (ED) and electron accepting (EA) monomers produce alternating copolymers [1-4]. The double bond of maleïc anhydride (MA) has strong electrophilic properties, so that the monomer can easily copolymerize providing that the comonomer is electron-donor. This is the case for cyclic olefins (internal olefins) : cyclopentene, cyclohexene, cycloheptene, cyclooctene [5, 6], norbornene [5, 7] thiophene or methyl thiophene [2, 8], indene [9] etc....

It was suggested that the alternating tendency could arise from the participation of 1:1 ED-EA charge-transfer complexes (CTC) in the propagation reaction [10]. In solution, when a CTC is formed between an ED an EA monomer pair, an equilibrium is obtained :

$$ED + EA \rightleftharpoons CTC \qquad (1)$$

and the constant K for this equilibrium is expressed as follows :

$$K = [CTC]/([ED] . [EA]) \qquad (2)$$

where [CTC], [ED] and [EA] are the concentrations of the respective species. Others studies [11,12] have revealed that free radical copolymerizations of MA and olefins do not involve significant participation of donor-acceptor complexes in the propagation steps, although the mixing of both monomers leads to a coloration due to formation of a charge-transfer complex. A simultaneous participation of both free monomers and charge transfer complex in the propagation reactions, is also accepted [4]. For the systems MA-cyclic olefins, a charge transfer complex formation is possible but its equilibrium concentration and stability are influenced by the donor or acceptor strength of the respective monomers and by resonance stabilization, steric effects, the nature of the solvent, temperature and feed composition.

The results from the literature, presented in a detailed review [13], show that the copolymers of MA with various cyclic olefin have been obtained in different conditions (method, concentrations, temperature, etc...).

The present study was undertaken in order to determine the effect of the nature of the cyclic olefin on the copolymerization process (copolymer composition, rate and yield of copolymerization) and to assess the role of a CTC in copolymerization. Additionally, we have studied the influence of the cyclic olefin on some properties of copolymers (intrinsic viscosity and glass transition temperature). For this reason in the present study the copolymers of MA with six cyclic olefins (cyclohexene-CX, cyclooctene 95 % cis-CO, cyclododecene-CD, norbornene-NB, indene-I and thiophene-T) were prepared in identical conditions (Table 1).

TABLE 1. Copolymerization of MA with cyclic olefins.

Feed composition (mole fraction of MA, f_{MA})	from 0.2 to 0.8
Total monomer concentration (MA + cyclic olefin), mole/l	1.5 + 1.5 = 3
Solvent	Dioxane
Temperature, °C	78
Initiator/concentration, mole/l	Benzoyl peroxide/4×10^{-2}
Time, h	10 or variable
Nonsolvent	Benzene/diethylether, 1/2 (V/V)

EXPERIMENTAL

All reagents were purchased by Aldrich; MA was recrystallized twice from chloroform, dried in vacuum at 30 °C and stored in a dry box. The cyclic olefins (CX, CO, CD, T and I) and dioxane were purified by careful distillation. Benzoyl peroxide was purified by recristallization from a mixture chloroform/methanol, 1/1 (v/v) and dried in vacuum at room temperature. ^{1}H NMR spectra for the monomers were recorded and compared with standard spectra. Radical copolymerizations were performed in dioxane as solvent in glass ampoules under a nitrogen atmosphere. The conditions of copolymerization are summarized in Table 1.

The copolymers were recovered by precipitation in a mixture 1/2 (V/V) benzene/diethylether, purified by precipitation from acetone, filtered and dried in vacuum at 40 °C.

The ^{1}H NMR spectra for the copolymers were recorded with a Bruker apparatus AM 300 (frequency 300, 13 MHz) using acetone d_6 as solvent with tetramethylsilane (TMS) as internal standard and monomer ratio in copolymer was determined by ^{1}H NMR integration.

Glass transition temperatures were measured with a DSC Setaram on powder samples of 10-15 mg at a heating rate of 10 °C/min. The IR spectra were recorded with a FT-IR 7PC Biorad apparatus. The chemical composition for the copolymers was also calculated from the C, H, O and S content determinated by elemental analysis. The viscosities of the solutions were measured at 25 °C with suspended level viscometer type Ubbelhode (kinetic energy corrections were negligible). The intrinsic viscosity $[\eta]$ was evaluated from the graph $\eta_{sp/C}$ vs. concentration (C), according to the known relation :

$$\eta_{sp/C} = [\eta] + k' \; [\eta]^2 \, c \qquad (3)$$

where k' is the Huggins constant and η_{sp} is specific viscosity.

RESULTS AND DISCUSSION

IR spectra of the copolymers MA-CX, MA-CO, MA-CD, MA-NB and MA-I show that MA is not hydrolized in the copolymerization process (the vibrations of the hydrolized MA were not observed at 1720 cm^{-1}). The chemical composition of the copolymers (molar fraction of MA in copolymers, F_{MA}) versus feed composition (molar fraction of MA, f_{MA}) is presented in Table 2. The results show that the monomers (MA and cycloolefins) have a tendency to give an equimolar copolymer. As the tendency of MA to homopolymerize can be considered negligible in this study (see the conditions in Table 1), we can suppose that the comonomers, also tend to alternate in the copolymer chain. This tendency is more or less marked depending on the system or on the feed composition.

For the same feed composition, $f_{MA} = 0.5$, this tendency increases slightly in the following order :

$$CO < CD \sim CX < I < NB \sim T.$$

TABLE 2 - Observed composition (fraction of MA in copolymers, F_{MA}) versus feed composition (f_{MA}) for the copolymers : MA-CX, MA-CO, MA-CD, MA-NB, MA-I, and MA-T.

Feed composition	Fraction of MA in the copolymer, F_{MA}					
f_{MA}	MA-CX	MA-CO	MA-CD	MA-NB	MA-T	MA-I
0.2	0.54	0.52	0.51	0.47	0.52	0.59
0.5	0.56	0.65	0.56	0.51	0.49	0.54
	0.59*	0.65*	0.55*	-	0.50*	0.57*
0.8	0.60	0.64	0.57	0.54	0.48	0.56

* Values calculated from ^{1}H NMR spectra

Fraction of MA in the copolymers MA-CO, MA-CX, MA-CD, MA-NB increases slightly with f_{MA} whereas it is pratically constant for different feed compositions for MA-T and MA-I copolymers. A yellow color was observed on mixing dioxane solutions of the acceptor MA with donor cyclic olefins indicating the formation of the charge-transfer complexes. In the case of thiophene the color is intense and was observed for all compositions but only for $f_{MA} > 0.6$ in the case of CO, CD and I. For the systems MA-CX and MA-NB a slight colouring was observed. In figure 1 we present the yield of copolymerization/h vs. feed composition, in Fig.2 are shown conversion-time curves (equimolar monomer mixtures) and in Tab.3 are presented the values of the copolymerization rate for the studied systems. The charge-transfer complexes are widely considered to play an active role in alternating radical copolymerization [10,12]. For the systems which form a 1:1 charge-transfer complex, if the sum of the concentration of ED and EA does not change, a maximum rate of copolymerization (or a maximum yield) is observed at an equimolar concentration f_{MA}~0.5) where the concentration of a CTC is expected to be highest [14]. In the case of MA-I, MA-CD, MA-CO and MA-NB copolymers, the maximum on the curve yield vs.feed composition is observed for

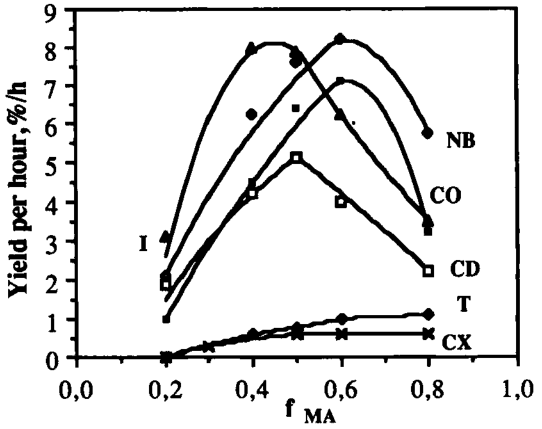

Fig.1: Yield per hour of copolymerization reactions versus f_{MA}

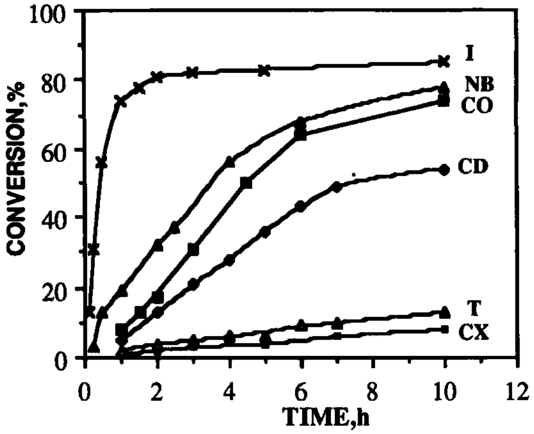

Fig.2: Conversion of the copolymerization reactions versus time (hours)

f_{MA}=0.5-0.6 and this fact may be, according [14], a support in accepting a role of CTC in copolymerization.

For the systems MA-T and MA-CX the curves yields vs feed composition do not show an obvious maximum. In this case we suppose that the role of the CTC is

TABLE 3 - Values of the copolymerization rate for the systems MA-cycloolefins and the glass transition temperatures, Tg, for the corresponding copolymers.

System	Rate of copolymerization mmol/L min*	Tg, °C
MA-I	2.75	133.2
MA-CO	0.30	127.9
MA-NB	0.28	not observed
MA-CD	0.18	125.7
MA-T	0.04	166.2
MA-CX	0.02	156.9

* from the slope of Fig. 2

diminished due to its stability or by simultaneous participation of both free monomers and CTC in the propagation reactions. The values of the copolymerization rate for the studied systems increase in the order (Fig. 2 and Tab.3) : CX < T < CD < NB < CO < I

An important difference for the copolymerization rate is observed between the studied systems. This difference can be explained by the values of the equilibrium constant K, equation (2) (K = 0.01 L/mol for MA-CX [15] and K = 0.32 L/mol for MA-I [16] and by the stability of the CTC in copolymerization. A similar explanation was formulated in the case of the systems MA-pyrrole and MA-methylpyrrole [17]. The role of the steric or electrostatic hindrance of the cycloolefin in the rigidity of the copolymer chains is illustrated by the relatively high values of the glass transition temperature (Table 3).

The variation of η_{sp}/C vs concentration of the copolymers solutions, equation (3), is presented in Fig. 3 (in dioxane) . The values of the intrinsic viscosity are small and increase in the order :

CX <T < CD < CO < NB < I

The same order is observed in the increase of the copolymerization rate indicating a similarity between the rate of copolymerization and molecular weight.

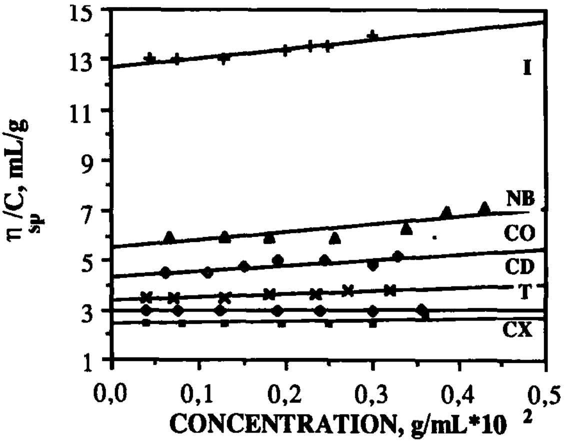

Fig.3: Reduced viscosities of the copolymers versus concentration of MA-cyclic olefins copolymer solutions (solvent: dioxane)

CONCLUSIONS

1- The rate of copolymerization depends on the nature of the cycloolefin and increases in the order : CX < T < CD < NB < CO < I

In the same order the intrinsic viscosity of the copolymers increases.

2- Fraction of MA in copolymers increases slightly with f_{MA} or is pratically *constant for different feed compositions.*

3- In the free radical copolymerization systems containing MA and cyclic olefins, the monomers have a tendency to alternate in the polymer chain. This tendency can be explained by the participation of CTC in copolymerization but the stability and reactivity of this complex depend on the nature of the cyclic olefin.

4- The values of the glass transition temperature are relatively high and increase in the order : CD < CO < I < CX < T

REFERENCES

[1] N.G. Gaylord, S. Maiti, B.K. Patnaik and A. Takahashi., *J. Macromol. Sci. Chem.*, A6, 1459 (1972).

[2] A. Cardon and E.J. Goethals, *J. Macromol. Sci. Chem.*, A5, 1021 (1971).

[3] M. Rätzsch, *J. Macromol. Sci. Chem.*, A 24, 517 (1987).

[4] D.J.T. Hill, J.J. O'Donnell and P.W. Sullivan, *Prog. Polym. Sci.*, 8 , 215 (1982).

[5] M. Kellou and G. Jenner, *Makromol. Chem.*, 180 1687 (1979).

[6] S. Murahashi, S. Nozakura and K. Yasufuku, *Bull. Chem. Soc.*(Jpn). 38 2082 (1965).

[7] U.S.Patent 3 280080 (1966) Union Carbide Co. invs. G.H. Potter and N.L. Zutty, Chem..Abstr.. 66, 3037 (1967).

[8] Y.A. Ragab, J. Polym. Sci., Part. C ; *Polym. Lett.* 28, 285 (1990).

[9] D. Tohru and M. Yugi, *Macromolecules*, 11, 270 (1978).

[10] S. Iwatsuki and Y. Yamashita, *J. Polym. Sci. Part.*, A 15, 1753 (1967).

[11] K. Dodgson,and J.R. Ebdon, *Eur. Polym., J.* 13, 751 (1977).

[12] Y.L. Spirin and T. Yatsimirskaya, *Vysokomol. Soed.* Ser., A 18, 755., Chem. Abstr. 85, 21961 (1976).

[13] J. Kroschwitz, Ed., Encycl. Polym. Sci. Eng., vol. 9 p. 225-94 Wiley New-York (1987).

[14] J.M. Solich and I. Rudnika, *Eur. Polym., J.* 24, 453 (1988).

[15] E. Tsuchida, T. Tomono and H. Sano, *Makromol. Chem.*, 151, 245 (1972).

[16] L. F. Kim, L. Stotskaya, B. Brenstel and V. Zubov, *J. Macromol. Sci. Chem.*, A 12, 1197 (1978).

[17] Y.A. Ragab, *J. Polym. Sci. Part.A ; Polym. Chem.* 29, 773 (1981).