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Terpolymerization Involving Maleic Anhydride and Dicyclopentadiene

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Summary

The results of radical ter-polymerization of maleic anhydride (MA), dicyclopentadiene (DCPD) and vinyl ter-co-monomers (vinyl acetate-VA, or butyl-vinyl ether-BVE) are discussed. The original objective was to obtain higher molecular weights, than the usual bi-component MA-DCPD copolymers. Some peculiar kinetic features have been put into evidence.

Introduction

DCPD represents a very interesting monomer, as it results as a waste in petrochemistry; on the other hand, DCPD contains two double bonds with distinct reactivities. The simplest idea for its valorization seems to be copolymerization. However, early works concerning the binary copolymerization of MA with DCPD [1, 2] have shown that only low-molecular products have resulted; also, their composition, structure as well as the suitable reaction mechanism presented a lot of contradictory features. In recent papers [3-7] regarding the system MA-DCPD, we have elucidated many of these aspects. For instance, it has been proved that low molecular weights correlated with small polymerization rates are both due to the degradative transfer with DCPD, regardless of some specific reaction conditions. Furthermore, the resulted copolymers exhibit an advanced thermal stiffness; indeed, there are no well-defined physical transitions in the temperature range studied, provided that their chemical structure is still maintained.

All these above mentioned findings, drastically restrain the potential practical uses and consequently, the utilization of DCPD through radical binary copolymerization. These facts have led to the idea of submitting DCPD to a ternary copolymerization of the type donor 1 (DCPD) – donor 2 (D_2) – acceptor (MA); however, D_2 should fulfill some indispensable requirements:

- To exhibit a strong tendency towards copolymerization with MA;
- This copolymerization must take place quite rapidly, forming products with high molecular weights, thus compensating the effect produced by the degradative chain transfer with DCPD;

- The new repeat units should be flexible enough, so that to diminish the conformational stiffness of the diads MA-DCPD.

Among the usual monomers fulfilling the aforementioned conditions [8] we have selected *n*-butyl-vinyl ether (BVE) and vinyl acetate (VA). The two monomers are significantly different both by their capacity toward homopropagation, or autotransfer; on this basis, some effects in their ternary copolymerization with MA-DCPD, might be anticipated.

The main aim of the present work was to check, whether the predicted effects on the molecular weights are (or are not) corroborated with experimental data.

Experimental

Materials

MA, DCPD and dioxane (D), used as solvent in copolymerization, have been purified according to previously described procedures [3-7]. BVE (Merck) has been used as such, while VA was purified by rectification. Aso-iso-butyro-dinitrile (AIBN) was submitted to recrystallization from a methanol/chloroform (1/1 vol) mixture.

Instruments

Copolymer composition has been calculated by elemental analysis (C, H, N); this method has been chosen, as the difference between the monomer composition is far higher than the standard error inherent to analysis. Molecular weights were appreciated by GPC (a Waters 510 apparatus- tetrahydrofurane as solvent).

Polymerization

Polymerization tests were carried out in vials, under a nitrogen cushion. All conversions were ascertained gravimetrically in a classical manner; therefore, precipitation of the reaction mixture took place in ethyl ether, followed by extraction (to remove unreacted monomers), drying in vacuum etc.

Results and discussion

The first tests have put into evidence the relationship between ter-polymer composition and monomer feed composition (MA-DCPD-BVE), for various conversions. As the system contains two donor monomers (BVE and DCPD), and an acceptor one (MA), the molar fraction of MA in monomer feed was kept at 0.5; for that reason, only the ratio between the two donor monomers has been modified. The results, starting from different monomer feeds are illustrated in figure 1.

For an easy comparison, we have kept the same reaction conditions (total monomer concentration of 3.5 mol/l and reaction temperature 80^0C) as those previously used for homogeneous binary copolymerization [3, 4] for the pair MA-DCPD. For each sample, elemental analysis was performed; the results, concerning the composition of products are presented in table 1. Obviously, the content in nitrogen (due to terminal groups) is placed far below the standard errors and, therefore, cannot be used to appreciate the polymerization degree; even so, the percentages obtained are around ten times lower, than those recorded in the binary copolymerization of the pair MA-DCPD, thus witnessing the presence of products with a higher molecular weight.

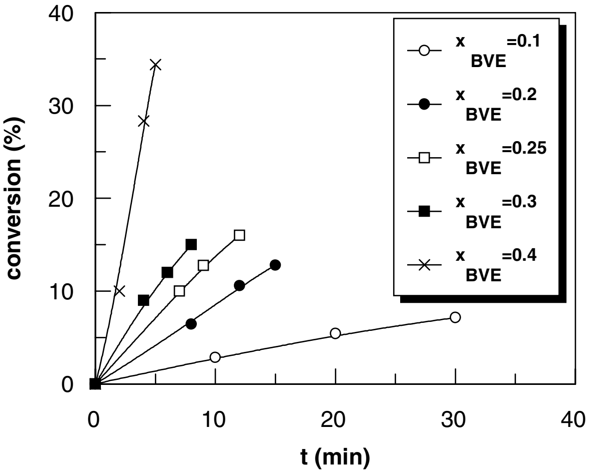


Figure 1. Kinetics of ter-polymerization for MA-DCPD-BVE (x_{BVE}- molar fraction of BVE [AIBN]=10^{-2} mole/l; [M_0]=3.5mole/l; T=80^0C)

Table 1. Results in terpolymerization of the system MA-DCPD-BVE ([AIBN]=10^{-2} mole/l; [M_0]=3.5mole/l; T=80^0C)

x_{BVE}	x_{DCPD}	Conversion (%)	C (%)	H (%)	N (%)	X_{MA}	X_{BVE}	X_{DCPD}	R_{p0} (mole/l*min)	M_n
		2.85	68.50	6.99	0.047					
0.1	0.4	5.43	68.93	7.18	0.050	0.49	0.33	0.18	$1.65*10^{-3}$	6800
		7.14	68.23	7.45	0.030					
		6.43	66.49	6.96	0.022					
0.2	0.3	10.59	66.06	6.62	0.023	0.51	0.35	0.14	$8.90*10^{-3}$	23700
		12.79	66.50	6.72	0.021					
		10.00	65.38	7.01	0.028					
0.25	0.25	12.75	65.28	6.95	0.030	0.5	0.39	0.11	$3.17*10^{-2}$	31300
		13.73	65.47	7.03	0.022					
		9.10	61.95	6.92	0.036					
0.3	0.2	12.12	62.09	7.02	0.034	0.5	0.46	0.04	$5*10^{-2}$	60000
		15.35	61.89	7.1	0.030					
		10.00	60.42	7.05	0.034					
0.4	0.1	28.00	60.62	6.94	0.040	0.50	0.49	0.01	$2.61*10^{-1}$	107400
		34.00	60.48	7.01	0.029					

A first remark is that ter-polymer composition depends on monomer feed composition, but apparently is not influenced by conversion; this statement is valid at least in the somewhat narrow range of monomer feed compositions that we have investigated.

Based on these results, we have drawn the Gibbs-type ternary diagram as illustrated in figure 2; it may be noticed that in all situations, copolymer composition is enriched in ethereal units, in comparison with the initial monomer feed composition.

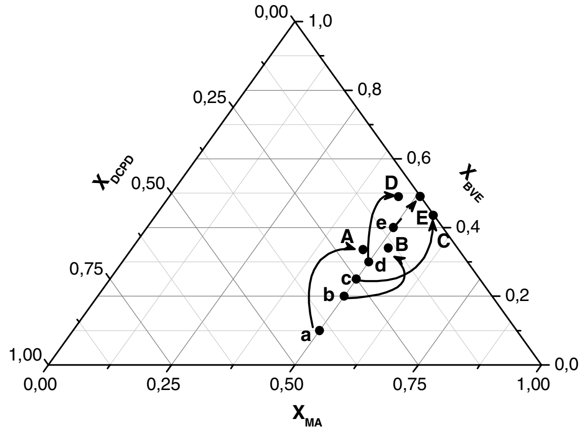


Figure 2. Gibbs-type diagram for copolymer composition in the system MA-DCPD-BVE
a: x_{BVE}=0.1 ; b: x_{BVE}=0.2 ; c: x_{BVE}=0.25 ; d: x_{BVE}=0.3 ; e: x_{BVE}=0.4 (monomer feed composition), A, B, C, D, E (copolymer composition)

The growing of the initial reaction rate (see table 1) for monomer feeds rich in BVE might be explained by the increase of the propagation/transfer ratio, with the decrease in DCPD content; furthermore, the variation of molecular weights is also convergent with this explanation. According to literature [2, 9], both pairs MA-DCPD and MA-BVE react in binary copolymerization not only as "free" monomers, but also through charge transfer complexes (CTC); obviously, the proportion of each mechanism depends onto the equilibrium constant between donor and acceptor. The corresponding value for the system MA-DCPD (K_2=0.06 l/mol) [2], is around ten times smaller, than for the system MA-BVE (K_1=0.56 l/mol) [9]. Recognizing that both mechanisms are valid, the explanation for the enriching in ethereal units is given through the higher reactivity of CTC_1 (MA-BVE) in comparison with DCPD, or CTC_2 (MA-DCPD).

Based on the above statements, a simplified kinetic model (involving CTC_1 and CTC_2) may be written, where MA=M_1, BVE=M_2, DCPD=M_3:

$$\begin{aligned}
&\sim\overset{\bullet}{M}_1 + CTC_1 \xrightarrow{k_{1C1}} \sim\overset{\bullet}{M}_1\\
&\sim\overset{\bullet}{M}_1 + CTC_2 \xrightarrow{k_{1C2}} \sim\overset{\bullet}{M}_1\\
&\sim\overset{\bullet}{M}_1 + M_3 \xrightarrow{k_{13}} \sim\overset{\bullet}{M}_1\\
&\sim\overset{\bullet}{M}_3 + M_1 \xrightarrow{k_{31}} \sim\overset{\bullet}{M}_1\\
&\sim\overset{\bullet}{M}_3 + CTC_1 \xrightarrow{k_{3C1}} \sim\overset{\bullet}{M}_2\\
&\sim\overset{\bullet}{M}_3 + CTC_2 \xrightarrow{k_{3C2}} \sim\overset{\bullet}{M}_3\\
&\sim\overset{\bullet}{M}_2 + CTC_1 \xrightarrow{k_{2C1}} \sim\overset{\bullet}{M}_2\\
&\sim\overset{\bullet}{M}_2 + CTC_2 \xrightarrow{k_{2C2}} \sim\overset{\bullet}{M}_3
\end{aligned}$$

Using classical simplifying premises and the quasi-stationary postulate, one may obtain the corresponding equation (1) for copolymer composition.

$$\frac{dM_2}{dM_3}=\frac{K_1}{K_2}\cdot\frac{M_2}{M_3}\cdot\frac{(k_{1c1}\cdot k_{2c2}\cdot k_{31}\cdot K_2\cdot M_1+k_{13}\cdot k_{2c1}\cdot k_{3c1}\cdot K_1\cdot M_2+k_{13}\cdot k_{2c2}\cdot k_{3c1}\cdot K_2\cdot M_3)}{(k_{13}\cdot k_{2c2}\cdot k_{31}+k_{1c2}\cdot k_{2c2}\cdot k_{31}\cdot K_2\cdot M_1+k_{13}\cdot k_{2c2}\cdot k_{3c1}\cdot K_1\cdot M_2+k_{13}\cdot k_{2c2}\cdot k_{3c2}\cdot K_2\cdot M_3)} \quad \mathbf{(1)}$$

Equation (1) may be written in a more compact form:

$$\frac{dM_2}{dM_3}=\frac{K_1}{K_2}\cdot\frac{M_2}{M_3}\cdot\frac{(A+B\cdot M_2+C\cdot M_3)}{(a+b\cdot M_2+c\cdot M_3)} \quad \mathbf{(2)}$$

as M_1= constant, and M_3=1.75-M_2

$$\frac{dM_2}{dM_3}=\frac{K_1}{K_2}\cdot\frac{M_2}{1.75-M_2}\cdot\frac{[A+B\cdot M_2+C\cdot(1.75-M_2)]}{[a+b\cdot M_2+c\cdot(1.75-M_2)]} \quad \mathbf{(3)}$$

Where A, B, C, a, b, c are groupings containing propagation constants.

Equation (1) contains a large number of unknown kinetic parameters, difficult to be evaluated by experiment; accordingly, our first attempt consisted in a graphical simulation of equation (1). So, the number of parameters has been reduced, by introducing the dimensionless ratios:

$$C_1=\frac{k_{1c1}}{k_{1c2}};\ C_2=\frac{k_{13}}{k_{31}};\ C_3=\frac{k_{2c1}}{k_{2c2}};\ C_4=\frac{k_{3c1}}{k_{3c2}}; \quad \mathbf{(4)}$$

Several sets of parameters C_i have been used, the main selection criterion being adequate values for k_{ij}, based on known values gathered from literature [10-13]; in this respect, the ratios C_i used by us, go into the same category as other well known ratios (r_i, r_{ij}, C_M, C_s, etc).

Four simulated curves (alongside with experimental points) are presented in figure 3; all these concave curves are monotonously increasing, in the same manner as the experimental points, so that might be considered a qualitative proof for the kinetic model proposed. Both the slope, and the curvature strongly depend on C_i values; there is at least a set C_1-C_4 that may describe the process according to equation (1).

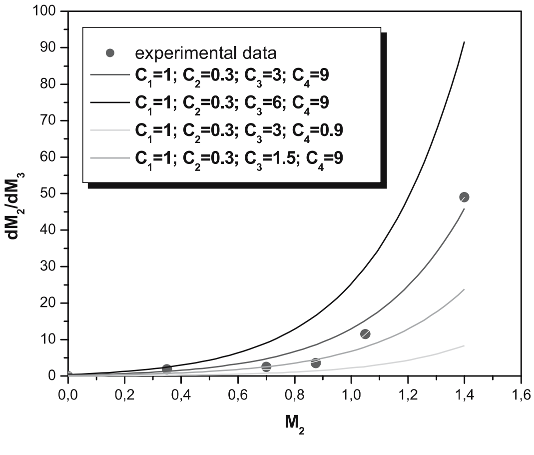
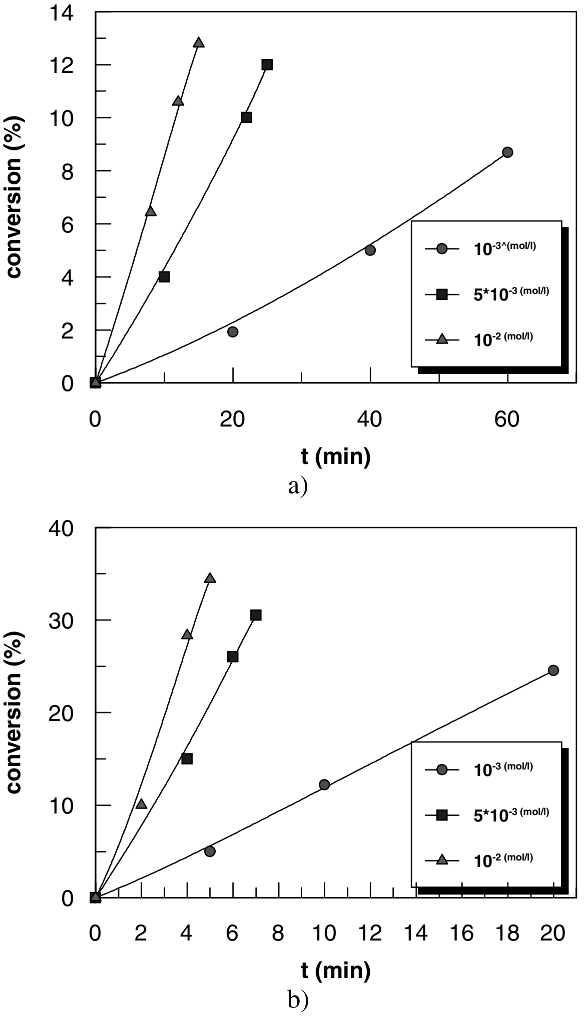


Figure 3. Ter-polymer composition (dM_2/dM_3) versus M_2 concentration in the initial monomer feed (-•- experimental data, as in table 1)

To put in evidence the influence of degradative transfer induced by DCPD on the process development, the partial reaction order with respect to initiator has been evaluated for two initial monomer feed compositions (x_{BVE}=0.2, x_{BVE}=0.4); indeed, the correlation polymerization rate versus initiation rate might bring important indications regarding the mechanism in the termination stage. The primary results are illustrated in figure 4; the straight lines, needed to calculate the partial reaction order, are presented in figure 5.

The data obtained suggest that as DCPD concentration increases, the apparent reaction order continuously advances from 0.5 (biradical termination, as for MA-BVE [14]) towards 1.0 (termination by transfer, as for MA-DCPD [5]). Consequently, it is difficult to write an exact equation (proper to be checked against experimental data) describing the copolymerization rate, in MA-DCPD-BVE ternary system.



a)

b)

Figure 4. Conversion versus time for different AIBN concentrations a) x_{BVE}=0.2 ; b) x_{BVE}=0.4 ($[M_0]$=3.5mole/l; T=80^{0}C)

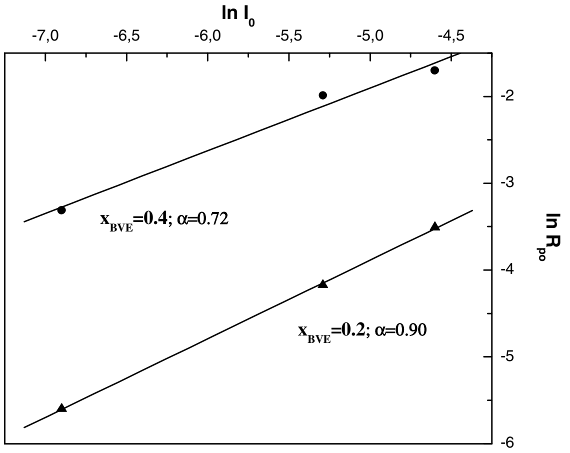


Figure 5. Partial reaction order with respect to AIBN: a) x_{BVE}=0.2 ; b) x_{BVE}=0.4

Completely different results have been obtained in the system MA-DCPD-VA; by comparison with the above discussed system, this time, both molecular weights and copolymerization rates are far lower (around one order of magnitude – see table 2).

Table 2. Results of ter-polymerization for the system: MA-DCPD-VA ([AIBN]=10^{-2} mole/l; [M_0]=3.5mole/l; T=80^0C)

x_{VA}	x_{DCPD}	Conversion (%)	C (%)	H (%)	N (%)	X_{MA}	X_{VA}	X_{DCPD}	R_{po} (mole/l*min)	M_n
0.1	0.4	3.45	76.10	6.10	0.150	0.58	0.03	0.39	$1.3*10^{-3}$	2800
		3.89	76.20	6.05	0.146					
		4.47	75.98	6.07	0.155					
0.2	0.3	2.61	72.38	5.58	0.130	0.52	0.14	0.34	$1.6*10^{-3}$	3400
		4.03	72.21	6.96	0.126					
		4.75	72.45	5.87	0.131					
0.25	0.25	2.91	66.38	5.46	0.121	0.48	0.26	0.26	$1.8*10^{-3}$	4800
		4.68	66.82	5.51	0.141					
		6.00	66.69	5.66	0.133					

Even if, by increasing the molar fraction of VA in monomer feed composition, copolymerization rate and molecular weight somehow augment, the effect is quite unimportant. It seems that the low reactivity of VA makes it unable to suppress the strong transfer induced by DCPD. Moreover, in the range $x_{VA}<x_{DCPD}$, the resulted copolymers contain a molar fraction of VA smaller than that in the initial monomer feed. Consequently, it may be said that by introducing VA, the expected improvements are quite moderate; the only remarkable result is the obtaining the ternary azeotropic composition $(D_1AD_2A)_n$.

Conclusions

- The systems MA-DCPD-BVE and MA-DCPD-VA respectively, have been submitted to terpolymerization, so that to obtain higher molecular weights, than for the binary copolymer MA-DCPD, in the conditions of superior reaction rates;
- Indeed, for the first system (MA-DCPD-BVE), higher reaction rates have been recorded, together with a significant enrichment in ethereal repeat units (with respect to initial monomer feed composition); this fact has been explained by the higher reactivity in propagation, shown by CTC_1;
- The proposed kinetic model is in good agreement with experimental data with regard to copolymer composition; however, an equation for the initial polymerization rate is difficult to be written, as the apparent partial reaction order with respect to initiator changes, as monomer feed composition changes as well;
- A spectacular increase (two orders of magnitude) of molecular weights has been noticed when introducing BVE (in comparison with the binary copolymer MA-DCPD); in due course, this system is to be investigated for practical purposes;

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