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Functionalized copolymers. Methyl methacrylate-(4-hexyloxy-1-phenyloxycarbonyl)-1,4-phenylene ethylene copolymers: synthesis, monomer reactivity ratios, thermal stability and solubility

Nancy Valdebenito, Fernando R. Díaz, Luis H. Tagle, Ligia Gargallo, Deodato Radic *

Departamento de Química Fisica, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Correo-22, Santiago, Chile

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Abstract

The synthesis and monomer reactivity ratios between methyl methacrylate and (4-hexyloxy-1-phenyloxycarbonyl)-1,4-phenylene-ethylene, a liquid-crystal monomer, were performed. Different starting monomer compositions were used to obtain copolymers with various compositions. Reactivity ratios r_1 and r_2 were estimated by the classical Fineman Ross and Kelen–Tüdős linear procedures and a non-linear method. These parameters were also estimated by using a computer program based on a non-linear minimization algorithm starting from the r_1 and r_2 values obtained by the above linear procedures. Copolymers were obtained by radical polymerization in THF solutions at 323 K under vacuum. Linear representation of the polymerization data seems to indicate a random copolymerization with some tendency to blocks formation. The thermal decomposition temperatures of the copolymers were determined by thermogravimetric analysis. The kinetic parameters associated with the decomposition process, show that there are a decrease of the thermal stability of the copolymers relative to the homopolymers.

Keywords: Copolymer; Liquid crystal; Monomer reactivity ratios; Thermal stability

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1. Introduction

In a previous paper [1] we have reported the synthesis and calorimetric properties of (4-hexyloxy-1-phenyloxycarbonyl)-1,4-phenylene-ethylene (HVB) which behaves as a liquid-crystal monomer with very well defined transition temperatures. On the other hand, we have synthesized the corresponding homopolymer (see Scheme 1) by free radical polymerization. The resulting polymer is insoluble in all the solvents studied. The homopolymer does not melt, but decomposes about 400°C. As the polymer obtained has not present liquid-crystal properties we had copolymerized the monomer with methyl methacrylate (MMA). By this process we can obtain a macromolecular structure containing the liquid-crystal monomer as comonomer. The effect of the composition of the copolymers on the solubility and on the thermal degradation can be analyzed. The chemical composition of such copolymers depends on the degree of incorporation of the comonomers and also on the relative reactivity between them. If we take into account the bulkiness of the side chain, it is possible to assume that steric hindrance should be an important factor to be considered in the copolymerization process and also on the thermal stability of the resulting copolymers. This

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* Corresponding author. Tel.: +56-2-6864741; fax: +56-2-6864744.

E-mail address: dradic@puc.cl (D. Radic).

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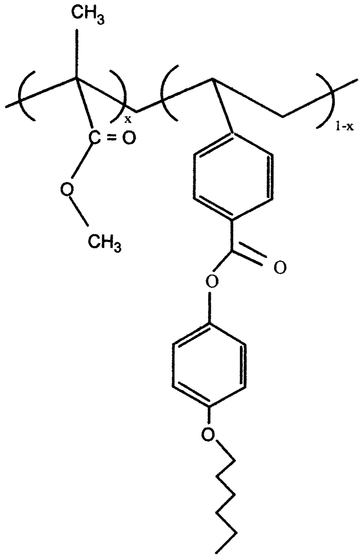

Scheme 1.

structural effect could be determinant in the comonomer sequence and distribution along the chain and therefore on the thermal properties of the resulting copolymer. It could be desirable to analyze this effect in order to get confidence about the structure and behavior of this kind of polymers.

The aim of the present work is the synthesis, determination of the monomer reactivity ratios and the analysis of the thermal stability and solubility of copolymers containing HVB. The effect of the insertion of a liquid-crystal monomer on an amorphous chain will be analyzed. The comonomer sequence of the resulting copolymer will be performed and discussed in terms of the chemical structure specific interaction and steric hindrance.

2. Experimental

Solvents from Aldrich or Merck were dried or distilled before using. Infrared spectra (IR) were determined in KBr pellets on a FTIR Bruker IFS 25 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded on a 200 MHz Bruker AC-200 instrument, using $CDCl_3$ as solvent and TMS as internal standard.

2.1. Synthesis of (4-hexyloxy-1-phenyloxycarbonyl)-1,4-phenylene-ethylene

The ester was synthesized according to the procedure previously reported [1] i.e. 10 mmol of 4-hexyloxyphenol were dissolved in 30 ml of dry THF and equimolar quantities of 4-vinylbenzoylchloride [2] and triethylamine were added to the solution, stirred at 5°C. After 4 h, the reaction was left to stand for 16 h at room temperature. The product was dissolved in CH_2Cl_2, washed successively with HCl 5%–water – NaOH 5%–water and dried over Na_2SO_4. The solvent was evaporated and the ester was purified by recrystallization from methanol. Further purification was achieved by chromatography (eluent:CH_2Cl_2-hexane 1:1); column material: silica gel 70-230 mesh. Yield 70%.

2.2. Copolymerization

Table 1 summarizes the relative amounts of monomers used for each copolymerization. 0.8 mg of α, α′-azo-bis-isobutyronitrile dissolved in 1.6 ml of dry THF were used for all the copolymerizations. Solutions contained in Pyrex-glass tubes were degassed using three freeze-degas-thaw cycles (10^{-4} mm Hg). Copolymerizations were achieved at 333 K until an increase of the viscosity of the solution was detected (about 26 h). The mixture was poured into methanol and reprecipitated from $CHCl_3$/methanol at least two times. The polymers were dried under vacuum at 313 K.

2.3. Thermogravimetric analysis

The thermogravimetric analysis were carried out in a Mettler TA-3000 calorimetric system equipped with a TC-10A processor, and a TG-50 thermobalance with a Mettler MT5 microbalance. The thermal degradation measurements were performed between 50 and 600°C at 20°C min^{-1} under N_2 flow.

3. Results and discussion

3.1. Synthesis and characterization of the copolymers

Copolymers from HVB and MMA of several compositions were synthesized according to a procedure previously described in Ref. [2]. Table 1 summarizes the

Table 1
Experimental quantities of monomers for copolymerization

Copolymer	$M_1 \times 10^4$ (mol)	$M_2 \times 10^4$ (mol)	Conversion (%)
1	0.32	0.08	33.7
2	0.24	0.16	20.0
3	0.16	0.24	28.5
4	0.08	0.32	23.4
5	0.04	0.36	20.0

M_1 – HVB and M_2 – MMA.

relative amounts of the monomers used for each copolymerization and the conversions obtained for each copolymer.

Copolymer composition was determined by FTIR spectroscopy monitoring the intensity variation of the C=O band corresponding to the aliphatic ester group versus the aromatic ester group.

3.2. Solubility

The solubility of the copolymers was checked in a variety of solvents. Table 2 collects solvents and non-solvents for the copolymer. As can be observed the copolymer is soluble in wide variety of liquids where the homopolymer is insoluble.

3.3. Monomer reactivity ratios

In order to get confidence about the real structure and sequence of the obtained copolymer, monomer reactivity ratios, r_1 and r_2, were determined. r_1 and r_2 were estimated by the least-squares method according to Finemann and Ross (FR) [3] by plotting G against F according to the equation:

$$G = Fr_1 - r_2 \tag{1}$$

where the transformed variables are:

$$G = \frac{x(y-1)}{y} \quad \text{and} \quad F = \frac{x^2}{y} \tag{2}$$

x and y defined as

$$x = \frac{M_1}{M_2} \quad \text{and} \quad y = \frac{\mathrm{d}M_1}{\mathrm{d}M_2} \tag{3}$$

with M_1 and M_2 the monomer molar composition in feed and $\mathrm{d}M_1$ and $\mathrm{d}M_2$ the monomer molar compositions in the copolymer.

Table 2
Solvents and non-solvents for HVB-*co*-MMA

Solvents	Solubility
THF	+
dioxane	+
benzene	+
toluene	+
dichloromethane	+
chloroform	+
n-hexane	0
ethyl acetate	+
ether	+
acetone	+
ethanol	0
nitrobenzene	+

+ = soluble; 0 = insoluble.

Monomer reactivity ratios were also estimated by using the Kelen–Tüdős [4] (KT) procedure according to:

$$\eta = \left(r_1 + \frac{r}{\alpha}\right)\xi - \frac{r_2}{\alpha} \tag{4}$$

being η and ξ mathematical functions of mole composition ratios of the monomers in the feed and copolymer respectively. These parameters are defined as:

$$\eta = \frac{G}{\alpha + F} \quad \text{and} \quad \xi = \frac{F}{\alpha + F}$$

where α is an arbitrary constant:

$$\alpha = (F_l F_h)^{1/2}$$

with F_l and F_h as the lowest and highest values for F.

Therefore, by this way, plots of η against x should give straight lines which extrapolated to $\xi = 0$ and $\xi = 1$ gives $-(r_2/\alpha)$ and r_1 both as intercepts. This formalism allows better distribution of the experimental points along the η–ξ axes than those of FR procedure.

Monomer reactivity ratios were determined by the least-squares method according to FR and KT procedure as shown in Fig. 1. Table 3 summarizes, monomer compositions in the feed (M_1), in the resulting copolymer ($\mathrm{d}M_1$) and the corresponding x, y, F, G, η and ξ parameters obtained using Eqs. (2)–(4). Table 3 compiles the r_1 and r_2 obtained by FR and KT linear procedures.

Reactivity ratios of HVB and MMA was also determined using a computer program based on a non-linear minimization algorithm (NLMA), reactivity ratio error in variable method [5] starting from the values of r_1 and r_2 obtained by the straight-line intersection methods. Fig. 2 shows the 95% probability contour for r_1 and

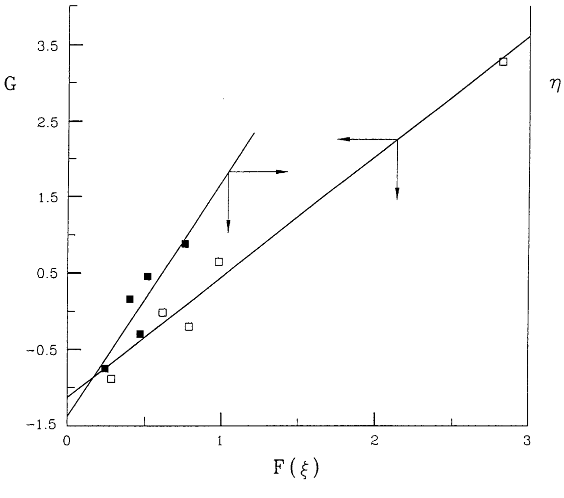

Fig. 1. FR (■) and KT (□) representation of the copolymerization parameters for HVB–MMA copolymers.

Table 3
Copolymerization data for MMA and HVB copolymers: composition in the feed (M_1), resulting composition (dM_1), x, y, F, G, F^{-1} and G/F as defined by FR [3] and η, ξ and α parameters as defined by KT [4]

Copolymer	M_1	dM_1	x	y	F
1	20	18	0.250	0.220	0.284
2	40	36	0.667	0.563	0.790
3	50	57	1.000	1.326	0.612
4	60	60	1.500	2.333	0.964
5	80	85	4.000	5.667	2.823

Copolymer	G	F^{-1}	G/F	η	ξ
1	−0.886	3.52	−3.12	−0.751	0.241
2	−0.518	1.266	−0.656	−0.307	0.469
3	0.246	1.633	0.402	0.163	0.406
4	0.856	1.037	0.888	0.460	0.519
5	3.294	0.354	1.167	0.886	0.759

$\alpha = 0.4752$.

Table 4
Monomer reactivity ratios r_1 and r_2 determined by FR, KT and NLMA

Method	r_1	r_2
FR	1.59	1.04
KT	1.69	0.66
NLMA	0.68	1.00

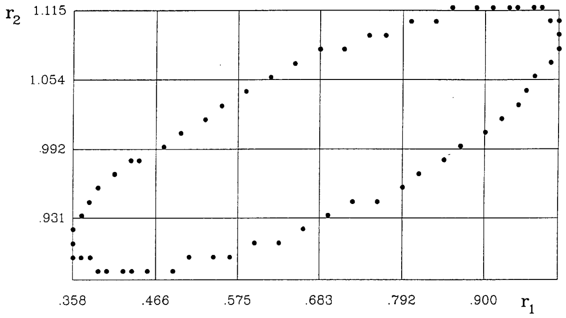

Fig. 2. The 95% probability contour for estimated r_1 and r_2 values for HVB–MMA copolymers.

r_2 starting from KT using the NLMA method for the probability contour.

If one of the reactivity ratios r_1 or r_2 are larger than the unity and the other is lower, there will be a shift in the composition, therefore the copolymer composition will be different from the initial one. This phenomenon is attributed to a larger reactivity of one of the monomers and therefore more units of the most reactive comonomer will be inserted in the macromolecular chain. On the other hand typical values r_1 and r_2 for radical copolymerization are lower than the unity. According to the data here reported by the KT method this would be the case. By this way it should be expected to observe some tendency to the formation of small blocks. Nevertheless, if the composition of the copolymer, relative to the feed is taken into account, it could be possible to assume a statistical distribution of the comonomers. The data of Table 4 allow us to conclude that in fact statistical copolymers are obtained. However, the FR results are not too different from the others. The explanation for these results can be achieved considering the relative stabilities of the propagating radicals. In the case of HVB there is a larger stability than in the case of MMA, but HVB is bulky, therefore both effects are balanced giving rise to a random copolymer with the tendency to the formation of small blocks of MMA.

3.4. Thermogravimetric studies

Fig. 3 shows the thermogravimetric curves of the copolymers decomposition. The thermal decomposition temperatures (TDT) of the copolymers were determined when they lost 10% of their weight, and are summarized in Table 5. The four analyzed copolymers showed a lower TDT than that obtained for the HVB homopolymer, due to the introduction of units with low side chain volume. The decrease of the TDT values of the copolymers does not show a direct connection with the MMA content, and are very similar between them.

The kinetic parameters of the thermogravimetric weight loss were calculated by using the kinetic equation (Table 5):

$$-\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = k_n(1-\alpha)^n \tag{5}$$

where α is the fraction of the sample weight at time t, and k_n the specific rate with kinetic reaction order n. The reaction rates $-(\mathrm{d}\alpha/\mathrm{d}t)$ were calculated using a differential technique with the heating rate (20°C min^{-1}) incorporated directly into the temperature versus sample weight-fraction data, according to the procedure developed by Wen and Lin [6]. The specific rates were calculated from the Arrhenius relation

$$k_n = A\exp\left(-\frac{E}{RT}\right) \tag{6}$$

where E is the activation energy, A the pre-exponential factor, T the absolute temperature, and R the gas constant. Eqs. (5) and (6) were combined and used in logarithmic form:

$$\beta = -\ln\left[\frac{(\mathrm{d}\alpha/\mathrm{d}t)}{(1-\alpha)^n}\right] = -\ln\frac{E}{RT} \tag{7}$$

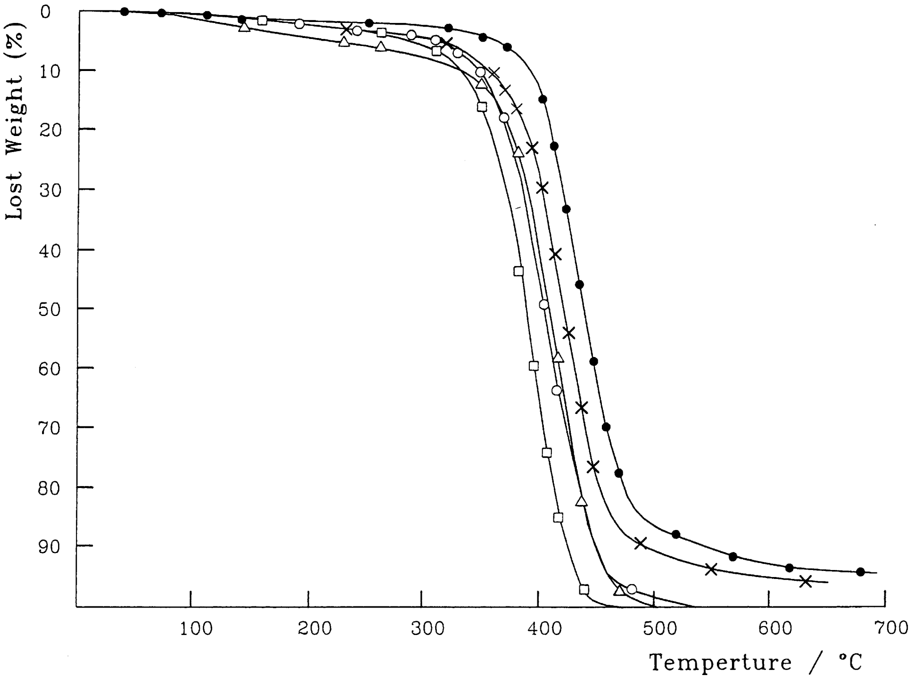

Fig. 3. Thermogravimetric profiles for homopolymers and copolymers of HVB–MMA. Copolymer 1 (□); copolymer 2 (△); copolymer 3 (○); copolymer 4 (×); HVB (●).

A computer linear multiple-regression program was developed to calculate the kinetic parameters E and A from linear least-squares fit of the data in a semilogarithmic plot of β versus $1/T$. Fig. 4 summarizes these results. The linearity of the plots was >0.995, although some scatter was detected at the beginning and end of each decomposition, which can be attributed to the difficulty to perform accurate measurements at the beginning and end of an experiment, as is frequently found in kinetic measurements.

The homopolymer of HVB follows a first-order kinetic instead of the zero kinetic order obtained for the copolymers. A zero kinetic order implies that $-(\mathrm{d}\alpha/\mathrm{d}t)$ is constant which means that when the mass of a sample is increased, the rate of loss of mass is constant as in a simple evaporation [7]. If we assume a first-order reaction for the copolymers, a non-linearity plot is obtained, which has been described as a change in the degradation mechanism and also a change in the activation energy [8]. Nevertheless, it is probable that the degradation of these copolymers also is a complex process, in which both monomeric units play some role. Furthermore, in this case, where there are two functional groups in two different repeating units, the degradation process can be composed of several stages that cannot be splitted in a clear range of temperature [9].

Therefore, assumptions concerning the reaction order and the constancy of the activation energy over a temperature range may be questionable. Moreover, kinetic treatment assumes that the residual weight of the

Table 5
TDT of HVB–MMA copolymers and kinetic parameters of the thermal decomposition

Copolymer	TDT (°C)	Range (°C)	n	E (kcal/mol)	A (seg^{-1})
MMA					
1	340	340–480	0	17.9	8.8×10^1
2	355	340–470	0	17.1	6.0×10^1
3	360	330–470	0	18.9	2.4×10^2
4	362	310–450	0	17.9	1.6×10^2
HVB	400	379–520	1	53.9	2.4×10^{13}

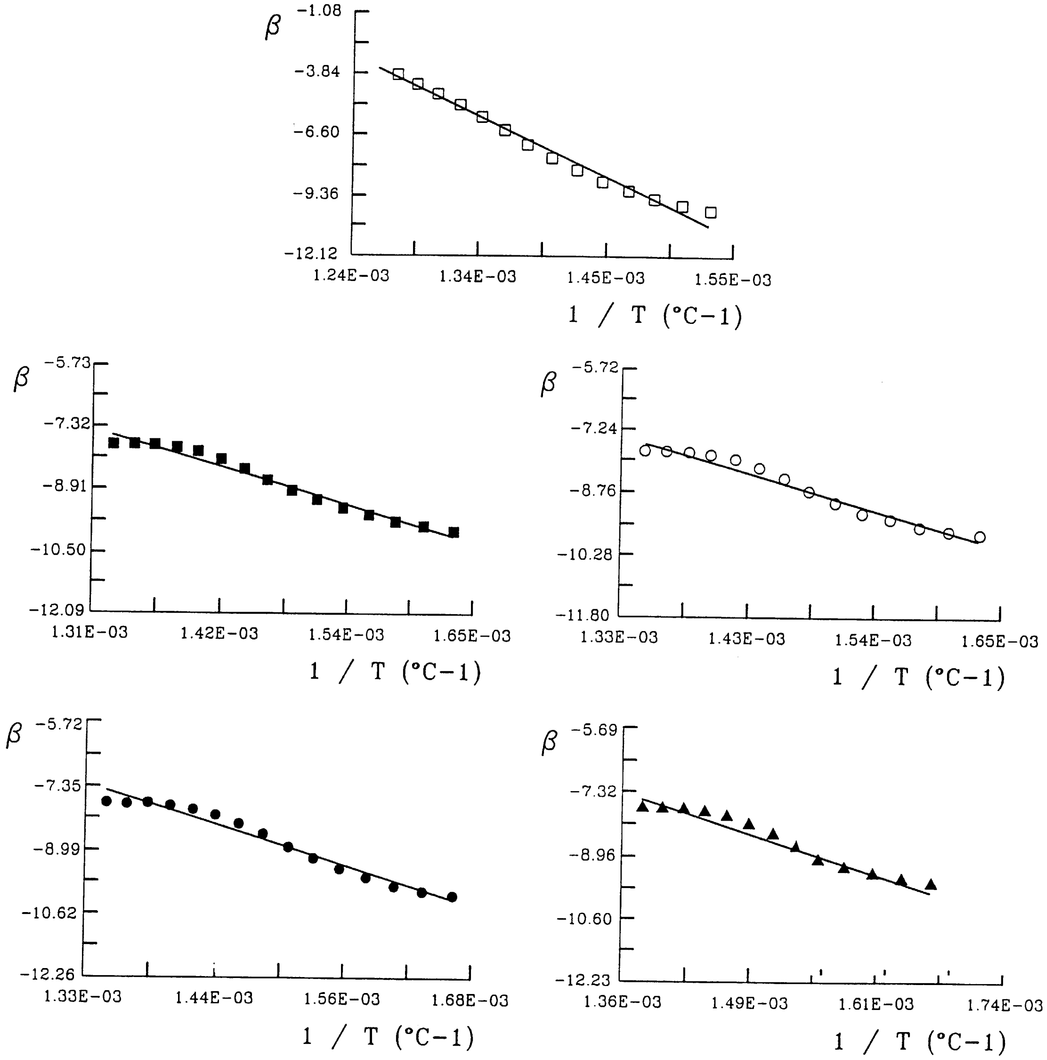

Fig. 4. Plots of β versus $1/T$ for copolymer 1 (□); copolymer 2 (■); copolymer 3 (○); copolymer 4 (●); and HVB (▲).

sample can be handled as a concentration, which is of doubtful validity [9]. In spite of the difficulties of interpreting the results of the kinetics parameters of the degradation of these copolymers, the thermal behavior allows us to know the temperature range in which they decompose and can be used, as well as the activation energy associated with the whole process.

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