ELSEVIER

Polymer 44 (2003) 1359–1365

polymer

www.elsevier.com/locate/polymer

The acid-catalysed polycondensation of 2-acetoxymethylthiophenes. Kinetics and mechanisms

Paola Stagnaro[a], Giovanna Costa[a], Franco Pioli[a], Alessandro Gandini[b,*]

[a]Istituto per lo Studio delle Macromolecole (ISMAC)-CNR, Sezione di Genova Via De Marini 6, 16149 Genova, Italy
[b]Matériaux Polymères, Ecole Française de Papeterie et des Industries Graphiques (INPG), BP 65, 38402 Saint Martin d'Hères, France

Received 6 August 2001; received in revised form 5 November 2001; accepted 7 November 2002

Abstract

This article describes the kinetics and mechanism of the acid-catalysed polycondensation of 2-acetoxymethylthiophene and its C3 and C5 methylated homologues. Numerous experiments were carried out by varying different parameters, such as temperature, solvent and acidic catalyst concentration. The presence of a methyl substituent at C3 or C5 position did not affect the qualitative features of the polymerisations, whereas their rates were enhanced owing to the donor character of the appended substituent. All reactions followed a first order behaviour with respect to the monomer and the activation energies were all around 50 kJ mol^{-1}. The DP of these products grew as a function of reaction time to reach values of about 40 at complete monomer consumption and thereafter chain growth could be reactivated by further monomer additions. Initiation in the presence of added polymer led to its grafting with a substantial increase in molecular weight. The evidence gathered suggests these polycondensations bear a living character.

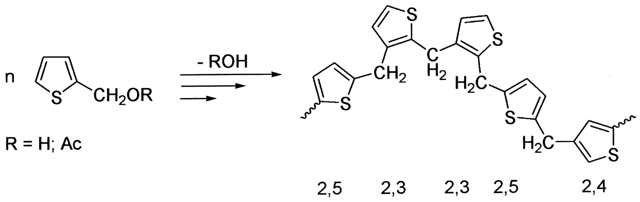
Keywords: 2-Acetoxymethylthiophenes; Acid-catalysed polycondensation; Kinetics and mechanism

1. Introduction

The acid-catalysed or heat-induced polycondensation of furfuryl alcohol has been extensively studied [1]. The basic step of these processes is a condensation reaction involving the OH group and the H atom at the C5 position of the heterocycle. However, the final products are black and cross-linked, instead of the expected linear colourless counterparts, because major side reactions, arising mostly from the dienic character of the furan ring, accompany the linear chain growth [2]. Benzyl alcohol is virtually unreactive under similar, or even more severe, conditions, which only lead to low yields of oligomers [3,4].

The thiophene homologue, viz. 2-hydroxymethylthiophene, should behave in an intermediate fashion since the corresponding heterocycle displays a chemical character which lies between that of furan (highly dienic) and benzene (highly aromatic). Only a brief note, appeared more than a decade ago, reported that a soluble poly(thienylene methylene) was obtained by the acid-catalysed self-condensation of this primary alcohol [5]. We tackled this and similar systems more recently by carrying a systematic investigation on the polycondensation of 2-hydroxymethylthiophene, its ester 2-acetoxymethylthiophene (**1**) and several homologues, induced by various Lewis and Brønsted acids [4], in which the emphasis was placed on the optimisation of the processes and the elucidation of the structure of the ensuing polymers.

The most relevant common features of these polycondensations [4] were (i) the formation of irregular sequences of $-Th-CH_2-$ units (Th = thiophene ring), in terms of the actual alkylation position on the heterocycle, viz. for monomer **1** and its alcohol



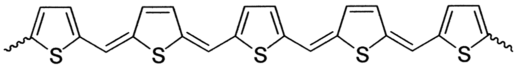
and (ii) the formation of conjugated moieties arising from reorganisation reactions associated with some of the units,

---

* Corresponding author. Tel.: +33-4-7682-6947; fax: +33-4-7682-6933.
E-mail address: alessandro.gandini@efpg.inpg.fr (A. Gandini).

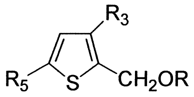
0032-3861/03/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(02)00854-6

which were converted into exounsaturated 2,5-dihydrothiophene structures, following the same mechanism previously unravelled with furfuryl alcohol [2], viz.



The major difference, however, with respect to the behaviour of furfuryl alcohol, was that the very modest dienic character of the thiophene heterocycle eliminated the possibility of macromolecular couplings by the Diels–Alder reaction and thus avoided the formation of cross-linked products which mar the polycondensation of the furan homologue.

The possibility of exploiting these systems as precursors to highly conjugated macromolecular architectures prompted us to pursue this investigation with the aim of acquiring the necessary insight into their kinetics and mechanisms as a precondition to a study on the actual materials. The monomers chosen for this work were **1**, 2-acetoxymethyl-3-methylthiophene (**2**) and 2-acetoxymethyl-5-methylthiophene (**3**), viz.



1: R = Ac; $R_3 = R_5 = H$
2: R = Ac; $R_3 = Me$; $R_5 = H$
3: R = Ac; $R_3 = H$; $R_5 = Me$

The acetates were preferred to the corresponding alcohols to avoid the accumulation in the reaction medium of the moisture formed in each condensation step, which was therefore replaced by acetic acid. The methyl substitutions were introduced in order to examine the alternative modes of condensation on the thiophene ring and their possible electronic and steric influence on the kinetics of this reaction.

2. Experimental

2.1. Monomers

2-Acetoxymethylthiophene (**1**), 2-acetoxymethyl-3-methylthiophene (**2**) and 2-acetoxymethyl-5-methylthiophene (**3**) were prepared, purified and characterized in our laboratory as previously reported [4].

2.2. Reagents and solvents

Methanesulfonic acid (Fluka, ≥99%), triethylamine (TEA, Fluka, 99.5%) and the two high purity solvents, 1,4-dioxane (diox) and 1,1,2,2-tetrachloroethane (TCE) were used as received. Pure commercial methanol was used as polymer precipitation medium.

2.3. General polymerisation procedure

The polymerisation reactions were carried out under nitrogen by dissolving the monomer in the solvent (a mixture of diox/TCE 75/25 v/v or pure TCE) and by adding thereafter, under vigorous stirring, the catalyst solution (1 M methanesulfonic acid in diox or TCE) to give 1.5 M solutions with respect to the monomer. In a typical polymerisation of monomer **1**, with $[\mathrm{Mon}]_0/[\mathrm{Cat}] = 10$, 3.00 ml (3.51 g, 22.5 mmol) of the monomer were dissolved in 9.75 ml of solvent; thereafter 0.15 ml (0.216 g, 2.25 mmol) of methanesulfonic acid in 2.10 ml of solvent were added. During both the addition and the polymerisation, the reaction mixture was kept at the desired constant temperature by keeping the vessel in a thermostated oil bath. Reactions were followed by GC and/or HPLC, as regards the rate of monomer consumption and by GPC as regards the evolution of the molecular weight of the polymer being formed. During each experiment, samples of the reaction mixture were regularly withdrawn, quenched with a slight excess of TEA and poured into a large excess of methanol. The resulting precipitate was separated by centrifugation, washed with methanol and vacuum dried to constant weight and the methanol solution was analysed for monomer and oligomeric species. The monomer conversion, measured by GC, was calculated according to the following equation:

$$\text{Conversion } \% = \left(1 - \frac{A_{0\ \mathrm{ref}} \times A_{\mathrm{t\ mon}}}{A_{\mathrm{t\ ref}} \times A_{0\ \mathrm{mon}}}\right) \times 100$$

where $A_{0\ \mathrm{ref}}$, $A_{\mathrm{t\ ref}}$ are the areas of the TCE peak (used as reference) and $A_{0\ \mathrm{mon}}$, $A_{\mathrm{t\ mon}}$ those related to the monomer, respectively, at the onset of the experiment and at the various withdrawal times. When HPLC was used, a calibration curve was first established relating monomer peak area to monomer concentration. The progressive decrease in monomer concentration during each experiment was then determined by injecting a known volume of the various methanol solutions corresponding to the sample withdrawals.

2.4. Polymer characterisation

Polymers were characterized by FTIR, ^{1}H NMR and UV-visible spectroscopy and by GPC. The latter technique was applied after calibration with standard polystyrene samples.

3. Results and discussion

The experimental conditions applied to the various polycondensations are summarised in Table 1.

Fig. 1(a)–(c) show the conversions vs. time plots related respectively, to runs 1–4 for monomer **1**, 8–11 for monomer **2** and 12–14, for monomer **3**. The corresponding first order plots are given in Fig. 2(a)–(c). The good linearity of all these plots indicates that the polycondensation of the three monomers followed a clear-cut first order

Table 1
Experimental conditions applied to the various polycondensations

Run	Mon.	$[\text{Mon}]_0/[\text{Cat}]$	Solvent[a]	Temperature (°C)	Time[b] (h)	M_p[c]
1	**1**	10	Diox/TCE	100	21	3100
2	**1**	10	Diox/TCE	80	24	3500
3	**1**	10	Diox/TCE	70	24	3700
4	**1**	10	Diox/TCE	60	48	n.d.[d]
5	**1**	10	Diox/TCE	40	156	3900
6	**1**	10	Diox/TCE	77	30	4000
7	**1**	10	Diox/TCE	70	26	3700
8	**2**	10	Diox/TCE	75	52	2600
9	**2**	10	Diox/TCE	60	52	3300
10	**2**	10	Diox/TCE	50	47	n.d.[d]
11	**2**	10	Diox/TCE	40	55	4900
12	**3**	10	Diox/TCE	80	25	1600
13	**3**	10	Diox/TCE	60	25	1600
14	**3**	10	Diox/TCE	40	28	1800
15	**1**	5	Diox/TCE	70	23	3900
16	**1**	20	Diox/TCE	70	72	3800
17	**1**	10	TCE	60	24	3800
18	**1**	10	TCE	40	23	4000
19	**1**	20	TCE	40	22.5	4100
20	**1**	40	TCE	40	33	4000
21	**1**[e]	10	TCE	60	24	6000
22	**1**[f]	10	TCE	60	48	4600/1000[g]

$[\text{Mon}]_0 = 1.5$ M; catalyst: MeSO_3H 1 M in diox or TCE.

[a] Diox/TCE 75/25 v/v.

[b] At which the run was stopped.

[c] Determined by GPC.

[d] Not determined.

[e] Aliquots of fresh monomer were added.

[f] Aliquots of fresh monomer were added starting from polymer recovered from another run.

[g] Values (double peak) refer to the THF soluble fraction (about 33 wt%).

behaviour with respect to them. The introduction of a methyl substituent at C3 or C5 induced a higher reactivity, which was more pronounced with the latter, viz. $k_3 > k_2 > k_1$. Fig. 3 shows the three Arrhenius plots which clearly suggest that the mechanisms associated with each system followed the same features, since the values of the activation energies were very similar. Table 2 gives the relevant kinetic data for this series of experiments in the mixed-solvent medium.

Table 2
Kinetic data for polycondensation of monomers **1**–**3**

Monomer	Solvent	Temperature (°C)	k (10^5 s^{-1})	E_a (kJ mol^{-1})
1	Diox/TCE	60	1.33	52.0
		70	4.33	
		80	5.00	
		100	11.83	
2	Diox/TCE	40	3.00	51.0
		50	5.33	
		60	9.67	
		75	21.33	
3	Diox/TCE	40	12.17	57.4
		60	68.17	
		80	145.67	
1	TCE	40	263.16	19.1
		60	420.33	

The equivalent runs conducted in TCE (17–20, Table 1) followed the same first order kinetic behaviour, but with much higher rate constants than those obtained in mixed solvents, e.g. a factor of over 300 at 60 °C, as shown in Table 2. The corresponding activation energy decreased to about 20 kJ mol^{-1}, i.e. more than a factor of two. These features are consistent with both the increase in the dielectric constant associated with the use of 100% TCE and the removal of the nucleophilic character of 1,4-dioxane, which strongly enhanced the reactivity and facilitated the formation of the activated (polar or ionic) complex.

The external order in acid was determined in two sets of experiments involving the two solvent media (3, 15, 16 and 18–20, respectively, Table 1). Fig. 4 shows the dependence of the first order rate constant on the acid concentration, which was 1.6 in mixed solvents and 2.3 in TCE.

The molecular weights (M_p, taken at the peak of the GPC tracing) associated with the end of the various runs are given in Table 1. An increase in the reaction temperature was always accompanied by a corresponding decrease in M_p. On the whole, the final M_p values related to the monomers followed the trend $M_{p1} \cong M_{p2} > M_{p3}$. In some instances,

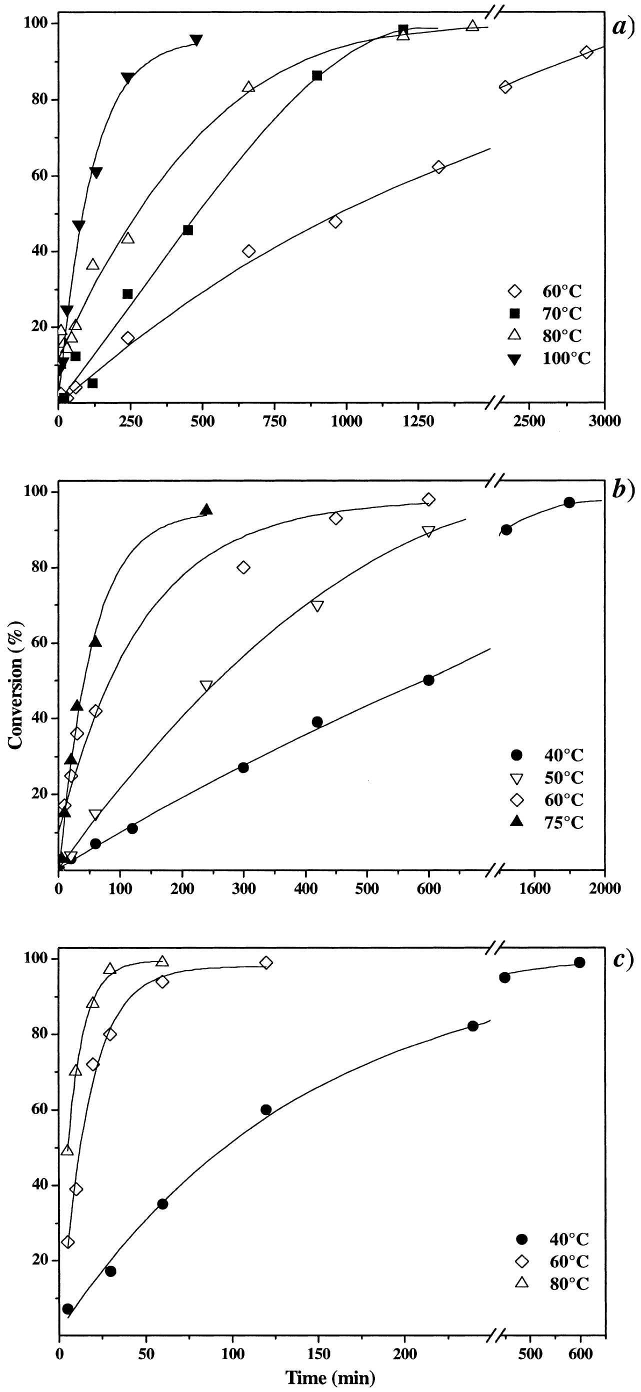


Fig. 1. Conversion vs time plots for the polycondensation of: (a) **1**; (b) **2** and (c) **3** in diox/TCE at various temperatures.

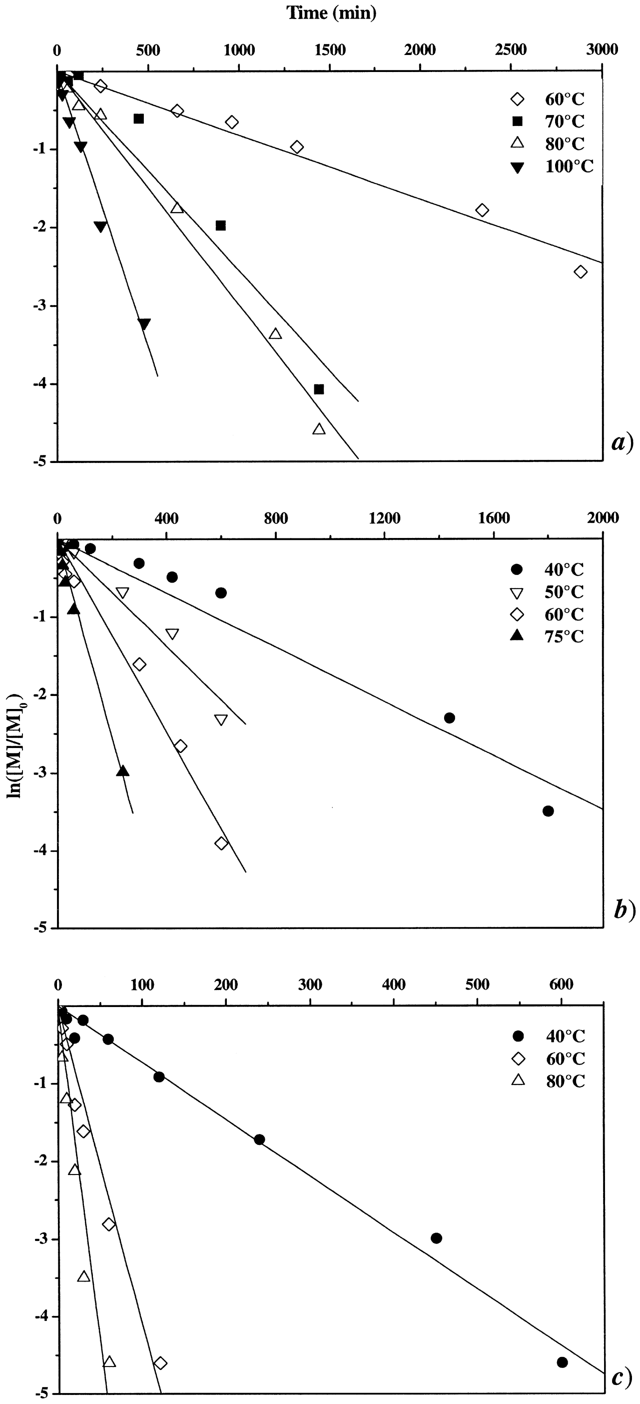


Fig. 2. Typical first order plots for the polycondensation of: (a) **1**; (b) **2** and (c) **3** in diox/TCE at various temperatures.

the reaction media were left for several hours to several days after complete monomer consumption, and samples were withdrawn in order to determine the M_p of the polymers. No significant change was noticed in any of these experiments, i.e. polymer–polymer condensation reactions did not take place to any appreciable extent.

The evolution of the molecular weight as a function of the reaction time was followed in several runs carried out in different conditions. Fig. 5 gives a plot which shows the progressive increase in DP with increasing monomer conversion for a slow polymerisation. With faster systems the DP reached its maximum value at lower conversion.

The spectroscopic analysis of the various polymers confirmed our previous conclusion [4] related to (i) the availability of all the free thiophenic carbon atoms to

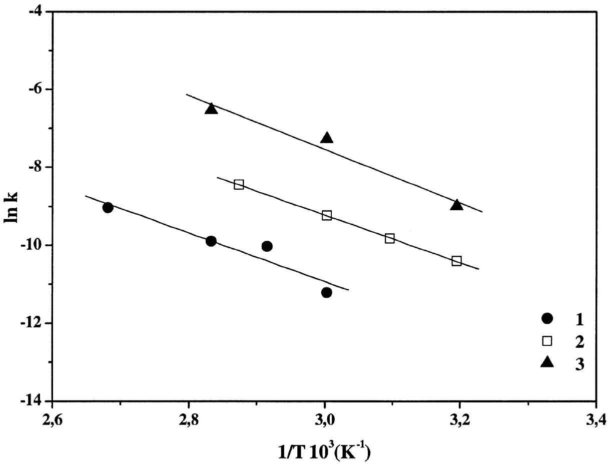


Fig. 3. Arrhenius plots for the polycondensation of monomers **1**–**3** in diox/TCE.

electrophilic substitution and (ii) the formation of conjugated sequences along all the different chains. Thus, both the irregularity of monomer unit enchainment and the alternating thiophene–dihydrothiophene sequences arising from the H^+/H^- abstraction mechanism [2,4], shown in the two polymer structures above, are common to the three monomers used in this study. The search for the acetate end groups was marred by their sensitivity to hydrolysis during polymer isolation, as shown by the difficulty in detecting them in the NMR spectra.

The sum of all the results gathered here provides reasonable evidence in favour of the following reaction mechanism.

3.1. Initiation

Two molecules of acid seem necessary to generate the active species by reacting with the monomer, viz.

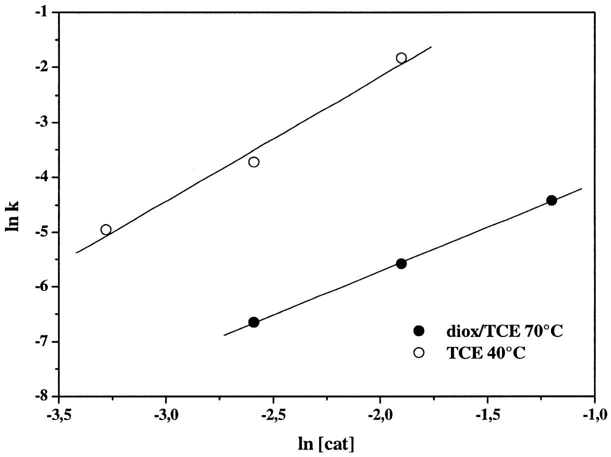


Fig. 4. Dependence of the first order rate constant on the acid concentration for the polycondensation of **1**: (●) in diox/TCE at 70 °C and (○) in TCE at 40 °C.

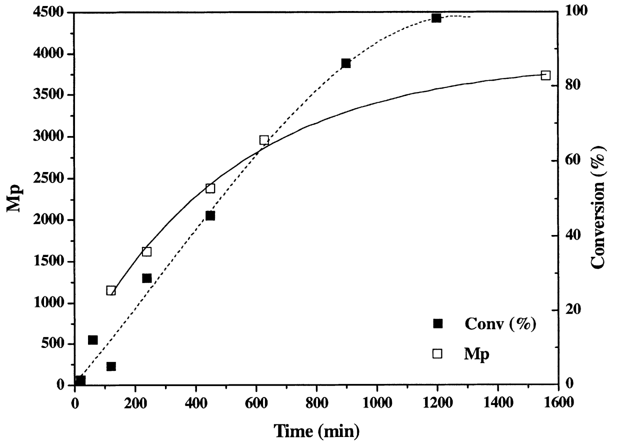
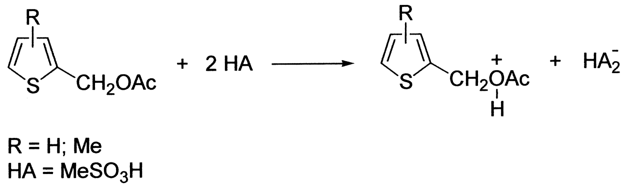


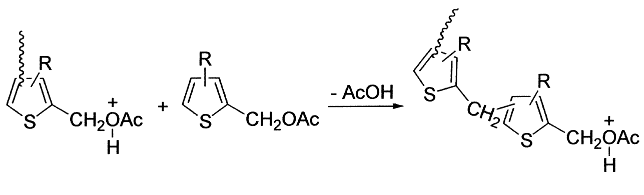
Fig. 5. M_p (left) and conversion (right) vs time plots for the polycondensation of **1** in diox/TCE at 70 °C.



The protonated acetate moiety seems a much more plausible structure for the active species than the $ThCH_2^+$ counterpart, which would be highly unstable, like the homologous benzyl and furfuryl cations. After this fast initiation, the concentration of active species appears to remain constant throughout the polymerisations, since they all exhibited first order kinetics with respect to monomer consumption.

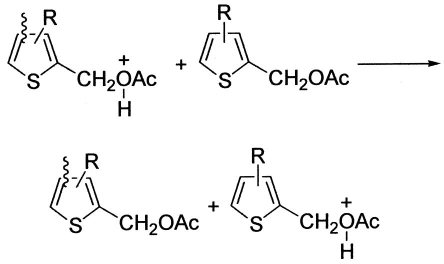
3.2. Propagation

The general mechanism for this reaction, common to all monomers, albeit with different rate constants, can be written as:



3.3. Transfer

The decrease in M_p with increasing temperature as well as the fact that monomer **3** was found to give the highest reactivity in terms of propagation, together with the lowest molecular weights, can only be rationalised by invoking the occurrence of transfer reactions. Indeed, termination reactions involving the disappearance of active species must be negligible in this context because of the good first order behaviour of all the runs, which implies, as emphasised earlier, that the concentration of chain carriers remained constant throughout these polymerisations. The mechanism proposed for the transfer reaction implies the same kinetics as the propagation, but the incoming monomer, instead of being alkylated by the active terminal unit of the growing chain, picks up the proton from it and starts a novel chain. This monomer transfer reaction can therefore be written generally as:



As with classical polyaddition systems, monomer transfer and propagation are kinetically equivalent and their relative importance is therefore directly defined by the ratio of the corresponding rate constants. In the present context, again as in typical free radical and cationic polymerisations, an increase in temperature favours the transfer reaction because its activation energy is higher than that of the propagation step. Additionally, a balance between steric factors and specific reactivity must be responsible for the different behaviour of the three monomers. In fact, although monomer **3** gave the highest rate of monomer consumption, it was also associated with the lowest molecular weights, thus suggesting that steric factors dominated in terms of favouring the transfer reaction, i.e. the increase in the propagation rate constant (compared with those of the other two monomers) was counterbalanced by a more important increase in the transfer rate constant.

The fact that M_p did not increase any further after the systems had reached complete monomer consumption, implies that the alkylation of a polymer chain by a macromolecular active species was a negligible event, if it did occur at all, probably because of steric hindrance. Thus, the only relevant propagation reaction is that sketched above, namely the interaction between an active species of any DP and the monomer. In order to corroborate this conclusion, two types of experiments were carried out consisting in (i) adding fresh monomer aliquots towards the end a given polymerisation (21, Table 1) and (ii) starting a polymerisation in the presence of a polymer recovered from another run (22). In both instances, a significant increase in molecular weight occurred as shown in Tables 3 and 4, respectively. In the second approach, the system developed very high molecular weights, to such an extent that the polymer started precipitating out of the reaction medium, as indicated in Table 4. Therefore, the molecular weight of the soluble fraction started decreasing when the proportion of precipitate was higher than the dissolved counterpart (Table 4).

Table 3
Molecular weights of the polymer being formed in run 21, Table 1

Time (min)	M_p	M_w
10	3700	4600
20	4400	5600
30	6100	7300
40	5600	7400
1440	6100	8300

Table 4
Molecular weights of the polymer being formed in run 22, Table 1

Time (min)	M_p	M_w
0	6000	8800
15	6300	10,900
30	6300	9700
45	7900	16,600
1440	8900[a]	19,800[a]
2880	4600, 1000[b]	9100[b]

[a] The withdrawal is partially insoluble in THF.

[b] Values referred to the THF soluble fraction (about 33 wt%).

The fact that the acid concentration did not affect the final DP of the polymer for a given system indicated that this value was determined by the ratio of the reaction rate constants related to propagation, k_p, and transfer, k_{trM}.

The initial increase in the polymer DP, particularly for slow reactions, can be rationalised in terms of the time necessary for the establishment of the stationary state after which the DP becomes governed by the kinetic ratio k_p/k_{trM}.

All the above evidence, qualitatively common to the three systems studied, points to a behaviour which can be rationalised as a polycondensation in terms of the mechanism of each growth step, but as a polyaddition in terms of its kinetic features and the fact that the only reactions leading to chain growth are those involving an active species and a monomer molecule.

4. Conclusion

This investigation constitutes a preliminary basic inspection of the kinetics and mechanisms of the polymerisation of **1** and its homologues **2** and **3** in view of a possible exploitation of the ensuing macromolecular structures as precursors to highly conjugated polymer architectures. Work is in progress to prepare these novel materials which might display useful properties in electronic and/or optoelectronic applications.

References

[1] Gandini A, Belgacem NM. Progr Polym Sci 1997;22:1203.
[2] Choura M, Belgacem NM, Gandini A. Macromolecules 1996;29:3839.
[3] Fournet F, Doucet A, Doucet-Baudry G, Janier Dubry JL. J Chem Res 1980;1001.
[4] Stagnaro P, Costa G, Gandini A. Macromolecules 2001;34:26.
[5] Uehara K, Kobatake Y, Tanaka M. Chem Express 1989;4:841.