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Polymerization of 4-vinyl biphenyl at advanced degrees of conversion

Issa A. Katime* and Teresa Nuño

Grupo de Nuevos Materiales, Departamento de Química Física, Facultad de Ciencias,
Universidad del País Vasco, Apartado 644, Bilbao, Spain

ABSTRACT

The bulk self-initiated polymerization kinetics, assuming total conversion, of the 4-vinyl biphenyl was determined by differential thermal analysis (DTA) in the temperature range 463-533 K. Likewise, the overall activation energy, E_A, and the polymerization enthalpies involved in the process have been calculated, as well as the overall rate constants and the reaction order with respect to the monomer concentration.

INTRODUCTION

Radical chain polymerizations of vinyl monomers are probably one of the most extensively studied subjects in polymer chemistry. Staudinger in the first quarter of the 20th century was the first to put forward a correct interpretation for the mechanism of free radical polymerizations, but the quantitative theory could only be developed after the establishment of the theory of chain reactions. Polymerizations at high degrees of conversion form no exception to the overall theory of radical chain polymerization, but the formation of the polymer takes place in this case under specific conditions. These ones include the high viscosity of the medium, the high concentration of the polymer in the system, the nature of the monomer, etc.

The relationship governing polymerizations at high degrees of conversion will differ from those ones valid in the case of reactions at initial degrees of conversion, and the theory developed for the latter case will not be valid for the former. Thus, the interpretation of advanced polymerization is more complicated than that one of polymerization at its initial stages.

In highly viscous media the relative importance of diffusional processes increases considerably and these processes may limit not only the chain initiation and chain termina-

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*Address for editorial correspondence and for offprint requests: Avda Basagoiti, 8-1° C, 48990 Guecho, Algorta Vizcaya, Spain

tion reactions, but also all other elementary reactions. For these reasons the interpretation of experimental results is very difficult. Polymerization at high degrees of conversion is of very considerable theoretical and practical interest, since it is the principle behind the production of many polymeric materials.

In recent years, differential thermal analysis (DTA) and differential scanning calorimetry (DSC), both equivalent techniques, have become increasingly important in the study of macromolecular chemistry.

These techniques have very important advantages which makes them specially usefull for the study of the kinetics of polymerization because its exothermic character can be easily followed by DTA or DSC, isothermally as well as dynamically.

In this paper we report a study of the bulk polymerization kinetics, at total conversion, of 4-vinyl biphenyl in the temperature range 463-533 K.

EXPERIMENTAL

4-vinyl biphenyl was purified by succesive crystallizations in methanol. The purity of the monomer was checked by IR and RMN spectroscopy.

The kinetics of polymerization have been studied in the temperature range 463-533 K using a Mettler TA-2000 differential thermal analyzer system, equipped with a scanning auto-zero device for obtaining a straight base line, which was calibrated using the temperature and heat of fusion of indium (T_m = 429.7 K and H = 28.0 $J.g^{-1}$).

The measurements were performed in aluminium crucibles filled with monomer quantities of aproximately 8 mg for each polymerization experiment. Dynamic and isothermal polymerizations were carried out by placing the aluminium crucibles containing the monomer into the furnace. Dynamic polymerizations allow us to establish the polymerization interval. Isothermal polymerization permits studying of the influence of temperature upon the polymerization rate and finding the overall activation energy.

The determination of the kinetic parameters has been carried out using a BASIC program written for a Commodore Amiga A-2000. This program plots dynamic and isothermal thermograms according to the integrated equations corresponding to different kinetic orders of reaction, in order to select the best reaction order for the monomer. Finally, the program calculates the kinetic rate constant from the slope of the straight line.

The DTA instrument was calibrated according to standard procedures. The absolute sample temperature was calculate using the following expression

$$T_{si} = T_{pi} - (dT_p/dT) + U_i/S$$

where T_{si} is the sample temperature at point T_i, T_{pi} is the program temperature at point T_i(°C), is an intrinsic DTA constant (0.411), dT_p/dT is the heating rate, U_i is the signal at point T_i (V) and S is the sensitivity of the thermocouple.

RESULTS AND DISCUSSION

Figure 1 shows the thermal behaviour of this monomer in the temperature range 363-533 K. As can be observed, the monomer fusion is produced at 387.4 K (endothermal peak). Likewise, in the temperature range 463-533 K appears an exothermal peak which corresponds to the temperature range over which the monomer suffers the self-initiated polymerization process. As can be seen, this kind of polymerization (when initiator is not used) starts at very high temperatures.

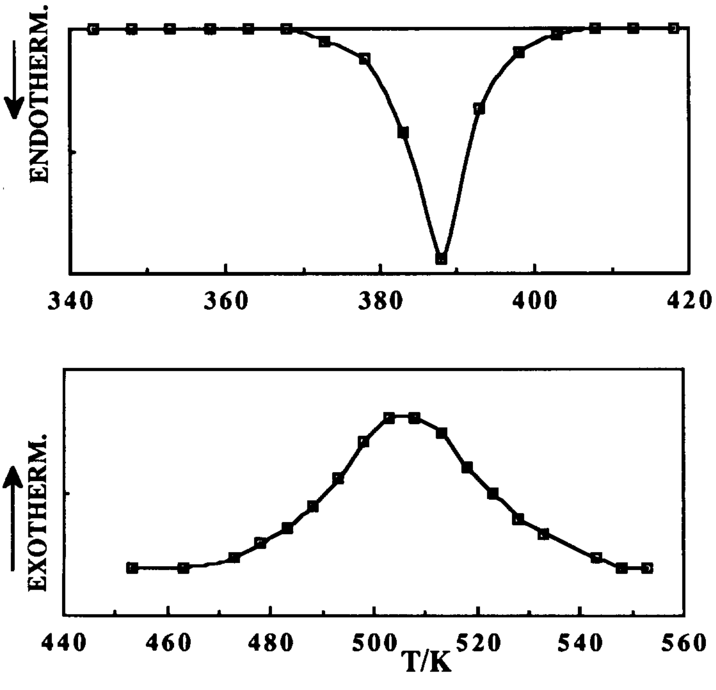

Figure 1. Thermal behaviour of 4-vinyl biphenyl in the temperature range 363-533 K.

From the different thermograms obtained in the temperature range 473-533 K the conversion rate at different times has been calculated, and from the obtained data we have determined that reaction order is 4/5 with respect to the monomer. In theory, for thermal self-initiated polymerizations the reac-tion order with respect to monomer should be 2. These differences may have their cause in the difficulty of monomers to diffuse towards the active centers (due to the great viscosity of the environment) and/or the appearance of other termination processes. Since the termination reaction involves two chain radicals, it might be expected that these radicals have to dif-fuse together before they can react. When this transport-diffusive process is the rate-determining step, it is then customary to refer to the termination reaction as being diffusion controlled. Furthermore, it is generally assumed that the termination step involves a three-stage process, that is, two chain radicals diffuse together so that certain segments are in contact (translational diffusion). Once the proximate pair has been formed, rearrangement of the radical chains may occur (intermolecular segmental diffusion) so that the reactive radical ends are close enough and are properly oriented for chemical reaction to take place. This concept of diffusion-controlled termination steps is largely due to North et al. (1961, 1961a, 1962, 1963).

Relying on this mechanism we have supposed for our case that termination is basically produced by intramolecular segmental diffusion of monomer units which form the macrodiradical, destroying themselves afterwards.

Therefore, the reaction order decrease might be partly explained by supposing the existence of a contribution more or less important of intramolecular segmental diffusion in our system. We have also observed this phenomenum for the mono alkyl itaconates (KATIME et al. 1988).

In Table 1 we can see the overall rate constants, k_{ov}, calculated in the temperature range 473-533 K, as it was expected they increase with temperature, it is interesting to point out the low value of these rate constants if we compare them with the obtained ones for the 1-vinyl imidazole at similar temperatures (KATIME et al. 1986). These differences may be due to the different way of initiation, because polymerization of 4-vinyl imidazole polymerization was initiated by thermal descomposition of AIBN.

Table 1. Overall rate constants, k_{ov}, for the 4-vinyl biphenyl polymerization in the temperature range 473-533.

T/K	473	478	483	493	503	513	523	533
k_{ov}	0.4538	0.5403	0.6131	0.6564	0.885	1.069	1.475	1.798

From the variation of overall rate constants with temperature by means of Arrhenius plot (see Figure 2) we have also obtained a 50.37 kJ.mol^{-1} value for the activation energy, E_A, of the polymerization process. This value can be very low compared with the obtained ones for the 1-vinyl imidazole (KATIME et al. 1986) and acenapthylene (KATIME et al. 1982) but it is concordant with the obtained ones for self-initiated po-lymerization processes of other vinyl monomers such as octyl acrylate (KATIME, NUÑO 1988), p-tertbutyl phenyl methacrylate (KATIME, NUÑO 1986) and n-vinyl succinimide (MORCELLET 1984).

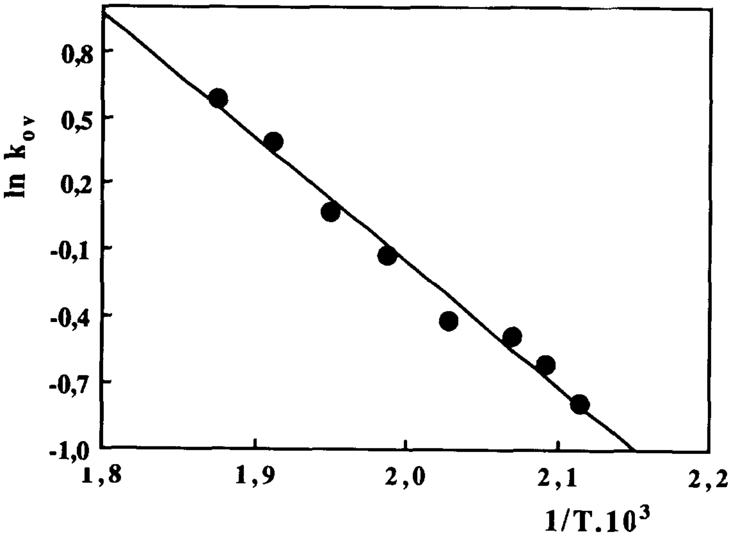

Figure 2. Arrhenius plot for the 4-vinyl biphenyl polymerization

Finally, we have calculated the polymerization enthalpy in the temperature range 478-533 K in order to study its dependence with temperature. The final result is shown in Figure 3. As can be observed in this Figure, there is a maximum located at 503 K which corresponds to the optimum self-initiated polymerization temperature for this monomer. It is necessary to point out that the obtained values are very low if we compare them with other vinyl monomers. This fact may be due to the conjugation of the C=C double bond with the phenyl rings of the substituent, which produces a monomer stabilization and the subsequent decrease in the polymerization enthalpies (ODIAN 1981). As it was discussed in the paper of the monoalkyl itaco-nates (KATIME et al. 1988), we can conclude that the use of this kind of monomers whose polymerization enthalpies are so low is very interesting because in this way it is avoided the problem of dissipating great quantities of heat from the system while polymerization, which is one of the greatest and most common problems for the polymeric material synthesis industries. This fact also contributes to the "Gel effect" or also named "Trommsdorff effect" (1948) elimination, which produces a self-acceleration in the polymerization process with the conse-quent variation of the molecular weight and molecular weight distribution of the obtained polymer.

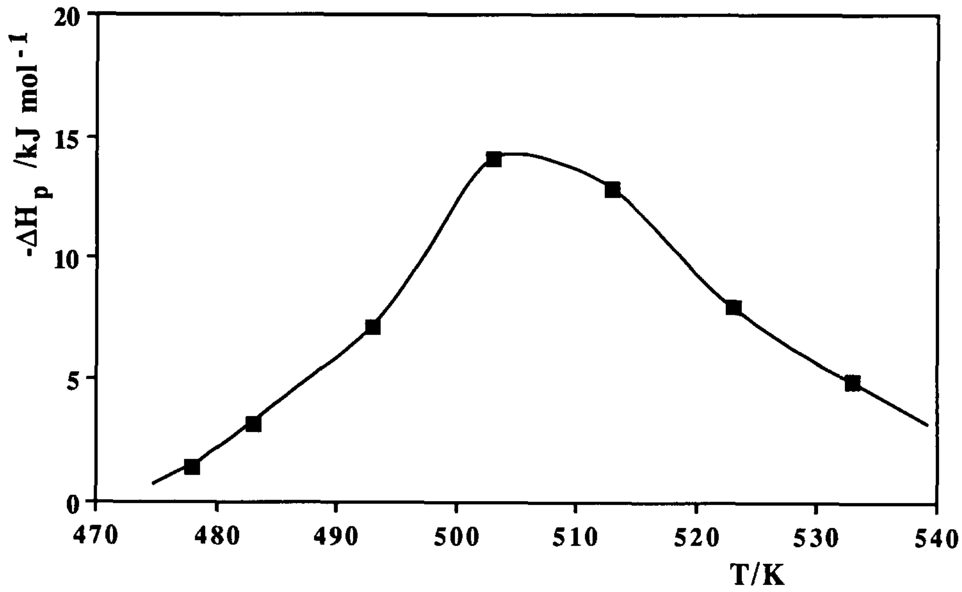

Figure 3. Polymerization enthalpies at constant temperature for the 4-vinyl biphenyl in the temperature range 478-533 K.

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