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THERMODYNAMIC DATA FOR SOME EVEN *TRANS* POLYALKENAMERS

G. Gianotti and A. Capizzi

Centro Ricerche Milano, Montecatini Edison S.p.A.,
Via Giuseppe Colombo 81, 20133 Milano, Italy

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Abstract—The thermodynamic quantities for the fusion of polyoctenamer, polydecenamer and polydodecenamer were investigated as a function of the *trans*-type double bond content. The method employed was that of Flory, which is concerned with the lowering of melting point in the presence of diluents.

The results obtained allowed us to evaluate by extrapolation the melting points and fusion enthalpies of pure transtactic stereoisomers. Comparisons were made with the related data previously reported for polyethylene and transtactic polybutadiene, considered as homologous members of the polyalkenamer series.

INTRODUCTION

Polyalkenamers, resulting from the stereospecific ring cleavage homopolymerization of cycloolefins,⁽¹⁾ constitute a homologous series of linear polymers; its members differ in the length of the methylenic sequences between the chain double bonds.

However, the physical properties of the different members of the series depend not only on this parameter, but also and predominantly on the type of steric configuration assumed by the double bonds during polymerization. In particular, the degree of crystallinity and the melting temperature of every member seem to be directly related to the amount of *trans* double bonds present in the chain.

Hence, any study intended to determine thermodynamic quantities on these polymers must necessarily take into account the steric characteristics of the samples examined and their homogeneity. This research has shown the extent to which the experimental values of melting point and fusion enthalpy depend on the *trans* double bond content; this allows an evaluation of these parameters for the pure *trans* stereoisomers.

Here we shall be concerned only with three even members of the homologous series, i.e. polyoctenamer, polydecenamer and polydodecenamer; we examined, for every polymer, several samples having different *trans* double bond contents, of controlled structural homogeneity.

In order to determine the enthalpy and entropy of fusion, the method adopted was that suggested by Flory⁽²⁾ based on the decrease of the melting point of the polymer in the presence of diluents.

EXPERIMENTAL

The samples used were prepared by polymerizing the single cycloolefins in the presence of catalysts based on $WOCl_4$ and $Al(C_2H_5)_2Cl$ under different polymerization conditions. The samples chosen were selected on the basis of the *trans* double bond content and steric homogeneity.

Infrared analysis

The *trans* double bond content was determined by i.r. spectroscopy on 0·5 per cent solution in CS_2, using the band at $10{\cdot}3\mu$.

Due to the pronounced tendency of cycloolefins with a higher number of carbon atoms to give predominantly transtactic polymers,(1) in the case of polydodecenamer the compositions cover only the range between 72 and 89 per cent of *trans* isomer. In the case of polydecenamer and polyoctenamer, the range is wider being 40–82 per cent in the case of polyoctenamer.

Preparation of the mixtures

The polymer–diluent mixtures (α-chloronaphthalene) were prepared by weighing convenient amounts of the components in glass vials, which were later cold-sealed under vacuum.

Homogeneity of the mixtures was ensured by frequently rotating the vials in an oven at 120°.

After cooling, four samples of about 5 mg were taken from different parts of each mixture. They were then enclosed in the special containers provided for volatile samples, and examined by differential scanning calorimetry (D.S.C.). The thermal schedule and the method for the melting point determination are the same as those described hereinafter for pure samples.

Following this procedure, the melting point determinations on the various samples fall within a range of ± 0·5° for each mixture.

Determination of the melting points

Melting points were determined by the Perkin–Elmer differential calorimeter DSC-1B. Runs were carried out on at least four samples of about 5 mg.

In order to avoid any possible influence of the previous thermal history on the melting temperature, a standard thermal treatment was used on all samples. In fact, after being placed in the calorimeter, the samples were kept at 120° for 10 min and then cooled at the rate of 8°/min until no further increase in crystallinity was registered. Soon after, the melting run was carried out by reversing the same thermal schedule; the final temperature of the endothermal peak was assumed to be the melting point. This procedure proved satisfactory for both accuracy and reproducibility.

RESULTS

Figure 1 shows the melting temperatures of the mixtures vs. the diluent concentration for the samples of different *trans* content. In all cases, their linear extrapolations to zero concentration agree with the values of melting temperature obtained for pure samples.

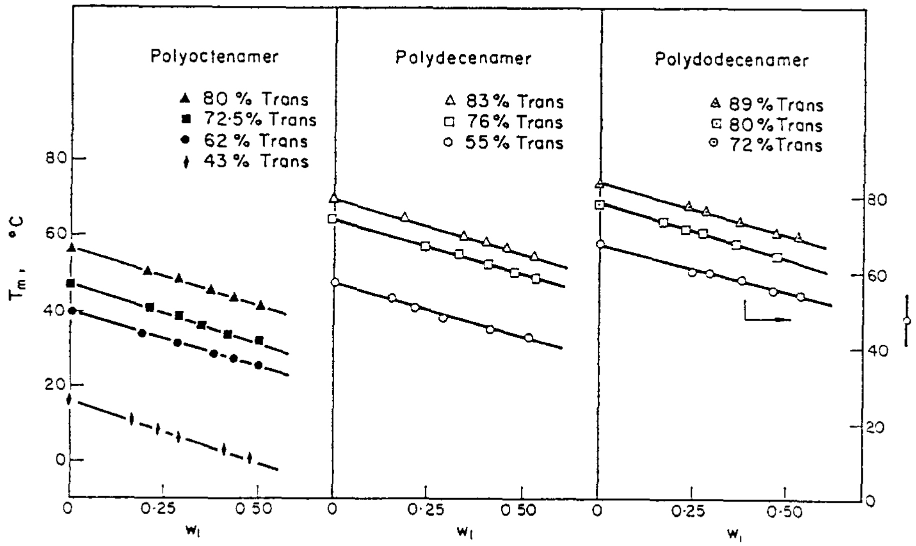

FIG. 1. Mixtures of polyalkenamers with α-chloronaphthalene. Melting temperatures vs. composition. (w_1 = weight fraction of diluent.)

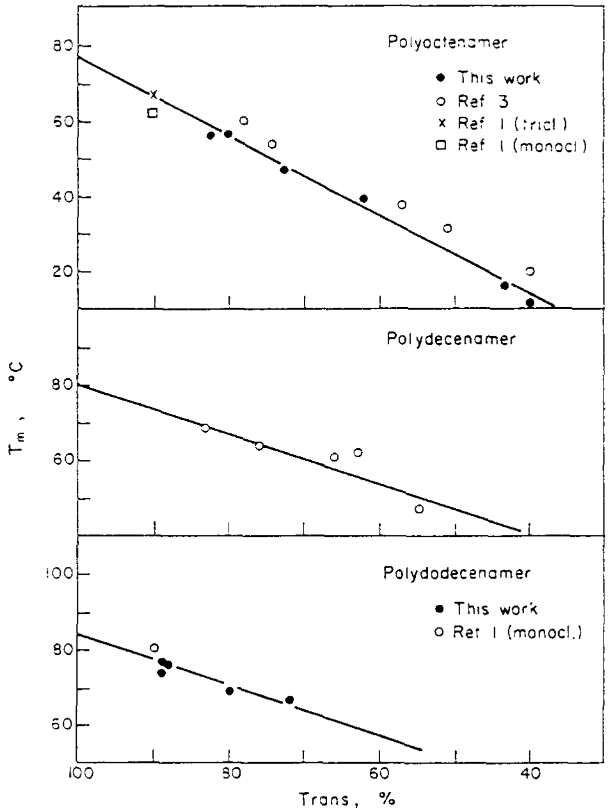

FIG. 2. Melting temperatures of polyalkenamers vs. their *trans* double bond content.

On the other hand, Fig. 2 shows the dependence of the melting point of pure samples on the *trans* double bond content for the three polymers studied by us. It also reports the data of other authors obtained by different techniques.(1,3)

The consistency between the experimental values of the melting temperatures of the pure products and those extrapolated from mixtures in α-chloronaphthalene indicates that the influence of the solvent on the polymorphism phenomena reported for polyalkenamers(1) is unimportant.

However, in order to be more sure of this, we undertook an accurate X-ray investigation. Figure 3 shows the Geiger spectra for the three pure polymers (having a higher *trans* content) and for their mixtures with α-chloronaphthalene of average composition ($w_1 = 0 \cdot 3$ to $0 \cdot 4$). As may be seen, polydodecenamer and polydecenamer are crystallized both when mixed with a diluent and in the pure state in the monoclinic modification.(1) On the contrary, in the case of polyoctenamer, the pure polymer shows the simultaneous presence of both monoclinic and triclinic modification, whereas the mixture shows the presence of the triclinic modification alone (disappearance of the reflection peak at $2\theta = 21 \cdot 5$). Since the two crystalline modifications show very similar melting points, their simultaneous presence in the pure polymer cannot be detected by D.S.C. analysis. This notwithstanding, it may be reasonably assumed that the temperature measured in this way corresponds to the higher melting modification

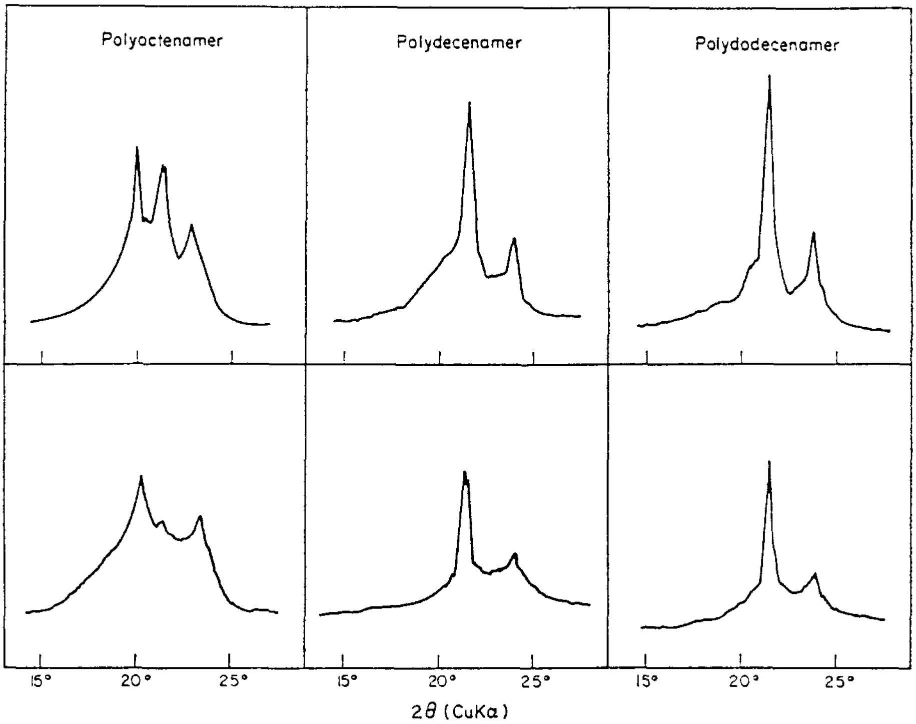

FIG. 3. X-ray diagrams for the three polyalkenamers (top) and their mixtures with α-chloronaphthalene (bottom).

and therefore to the triclinic modification,(1) which, in the case under examination, is just the modification observed in the mixtures with α-chloronaphthalene (see Fig. 3). Hence it would be possible to determine the thermodynamic parameters of fusion for the crystalline monoclinic modification of polydodecenamer and polydecenamer and for the triclinic modification of polyoctenamer.

Measurements could not be accomplished on the same crystalline modification for all three polymers: however, this is not a fundamental drawback to the possible conclusions.

In Fig. 4 we report the melting data of mixtures with α-chloronaphthalene of the three polyalkenamers of various degrees of purity treated according to the Flory equation:(2,4)

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u} \cdot \frac{V_u}{V_1} (v_1 - \chi_1 v_1^2) \tag{1}$$

where V_u and V_1 are respectively the molar volumes of the polymer repeating units and of the diluent; v_1 the volume fraction of the diluent, χ_1 the polymer–diluent interaction parameter and ΔH_u is the heat of fusion per mole of repeating units in pure polymer.

The ΔH_u values obtained from extrapolation show a considerable dependence on the steric purity of the samples.

Figure 5 shows the ΔH_u of fusion of the various samples vs. the content of *trans* double bonds.

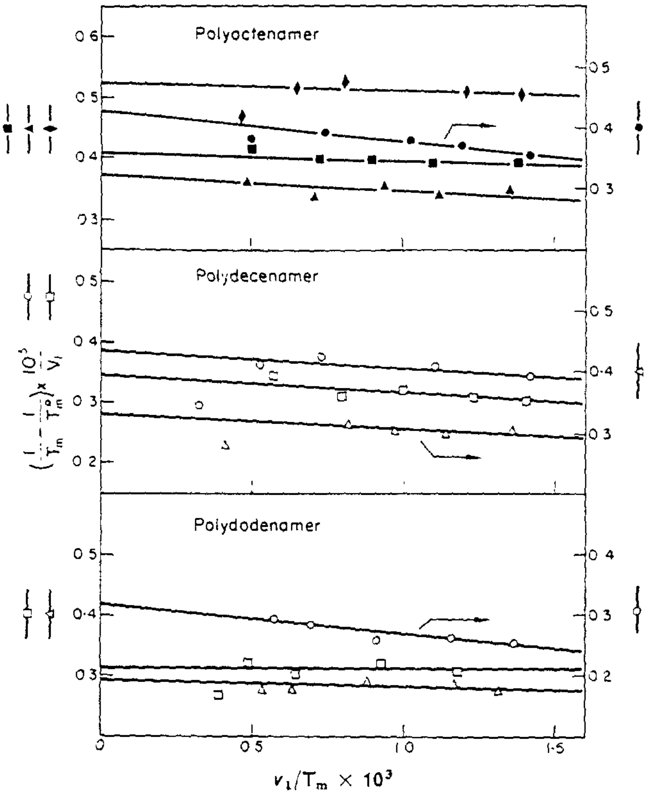

Fig. 4. Typical plots for the evaluation of fusion enthalpy (for symbols, see Fig. 1).

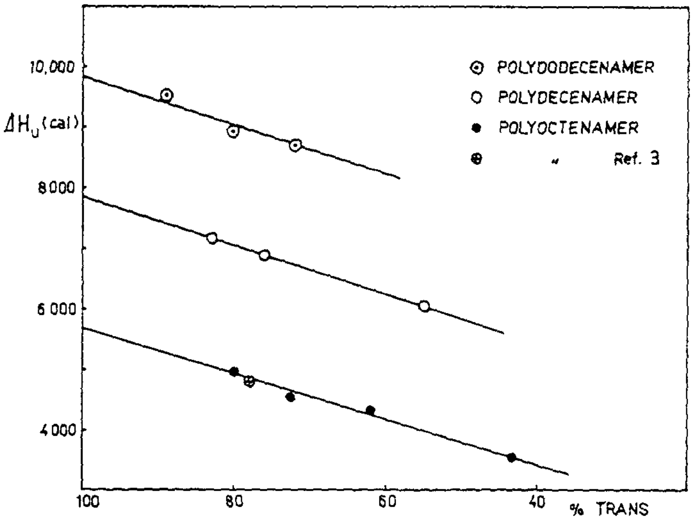

Fig. 5. Fusion enthalpies of polyalkenamers vs. the *trans* double bond content.

By an accurate examination of the experimental values, we may accept, as reasonable, a linear extrapolation for the evaluation of the ΔH_u of fusion of the three sterically pure *trans* polyalkenamers.

Table 1 lists these values and other thermodynamic quantities; they are compared with the data reported in the literature for polyethylene(6) and transtatic polybutadiene,(7) polymers structurally related to those studied here.

TABLE 1. THERMODYNAMIC PARAMETERS OF FUSION EXTRAPOLATED FROM SOME *trans* POLYALKENAMERS

Polymer	Crystalline modification	T_m (°K)	ΔH_u	ΔS_u	ΔS/bond	Reference
Polyethylene	Orthorhombic	411	1920	4·68	2·34	6
Polydodecenamer	Monoclinic	357	9840	27·60	2·50	*
Polydecenamer	Monoclinic	353	7850	22·20	2·47	*
Polyoctenamer	Triclinic	350	5680	16·20	2·32	*
Polybutadiene (I)	Pseudohexagonal	370	3300	8·90	2·90	7

* This work.

In this paper, we do not report the values of ΔH_u that could be obtained by the relationship between melting point and composition of copolymers(2) (see Fig. 2), first of all because of the well-known discrepancy between the sets of values supplied by the two methods(5) and secondly because we wished to get values directly comparable with those of the literature.(6,7)

It is interesting to compare the entropies of fusion of these polymers, rather than the enthalpies. In fact, since the main contribution to the entropy of fusion presumably derives from the increase in the number of configurational states of the chain segments during melting, ΔS_u should increase with the number of segments, which may be oriented independently, in the unit. Therefore, in order to have a common basis of comparison for the results obtained, we may divide ΔS_u by the number of bonds around which rotation is allowed.

The resulting values, reported in the last column of Table 1, are very similar and most of them range between 2·3 and 2·5 cal/deg/bond. The slightly higher value observed for *trans*tactic polybutadiene might result solely, as already reported,(7) from the higher contribution of volume entropy.

Due to the above remarks and to the confidence limits of the applied method, whatever other consideration, in order to attribute a precise structural meaning to the differences between the values, would be ambiguous.

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Résumé—On a étudié les grandeurs thermodynamiques correspondant à la fusion de polyocténamère, polydécénamère et polydodécénamère en fonction de la quantité de doubles liaisons de type *trans* présentes. On a employé la méthode de Flory qui étudie l'abaissement du point de fusion en présence de solvants.

Les résultats obtenus nous ont permis d'évaluer par extrapolation les points et les enthalpies de fusion des stéréoisomères transtactiques purs. Des comparaisons ont été faites avec les données précédemment fournies pour le polyéthylène et le polybutadiène transtactique, en considérant ceux-ci comme des membres homologues de la série des polyalkénamères.

Sommario—Vengono studiati i parametri termodinamici relativi alla fusione del poliottenamero, polidecenamero e polidodecenamero in relazione al loro contenuto in doppi legami di tipo *trans*.

E' stato impiegato il metodo di Flory basato sull'abbassamento del punto di fusione in presenza di diluenti. I risultati ottenuti hanno permesso di ricavare per estrapolazione le temperature e le entalpie di fusione degli stereoisomeri transtattici puri.

Si è fatto un confronto con i corrispondenti valori già noti per il polietilene e il polibutadiene transtattico, considerati come termini omologhi della serie dei polialchenameri

Zusammenfassung—Für das Schmelzen von Polyoctenamer, Polydecenamer und Polydodecenamer wurden die thermodynamischen Größen als Funktion des Gehalts an Doppelbindungen des trans-Typs untersucht. Dabei wurde die Methode von Flory angewendet, die sich auf die Herabsetzung des Schmelzpunkts in Gegenwart von Verdünnungsmitteln gründet.

Die erhaltenen Ergebnisse gaben uns die Möglichkeit, durch Extrapolation die Schmelzpunkte und die Schmelzenthalpien der reinen transtaktischen Stereoisomeren zu bestimmen. Die Werte wurden verglichen mit entsprechenden, kürzlich angegebenen Daten für Polyäthylen und transtaktisches Polybutadien, die als homologe Glieder der Polyalkenamer Reihe betrachtet werden können.