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THE GLASS TRANSITION IN POLY(3-Br-*N*-VINYLCARBAZOLE)

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ABSTRACT

The glass transition temperature of poly(3-Br-*N*-vinylcarbazole) has been determined by calorimetric studies. It has been found that T_g^∞ and K values of the Fox–Flory relationship show a dependence on heating rate. The activation energy conferred to the glass transition process has been determined and compared with that for cationic and radicalaric PNVC.

INTRODUCTION

Using differential scanning calorimetry (DSC), poly(3-Br-*N*-vinylcarbazole) (PBrNVC) samples were found to exhibit only one glass transition temperature T_g which has a linear dependence on $1/\overline{Mn}$ in terms of the Fox–Flory relation [1,2]

$$T_g = T_g^\infty - \frac{K}{\overline{Mn}} \tag{1}$$

where T_g^∞ is the T_g value at infinite molecular weight, K is a constant and $\overline{Mn}$ is the number average molecular weight. We have found that T_g^∞ and K depend on the heating rate. Variations in T_g^∞ and/or K values will determine changes in the T_g values.

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RESULTS AND DISCUSSION

The PBrNVC was synthesized from 3-Br-*N*-vinylcarbazole monomer using radicalaric polymerization as previously described [3]. The polymer was purified and then fractionated by precipitation with absolute methanol from benzene solution and four monodispersed samples were chosen for this study. Their molecular weights were determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) at 25 °C using a Waters-150 liquid chromatograph according to the universal calibration method. The intrinsic viscosity (η) of each fraction was measured at the same temperature as that at which the GPC experiments were performed. The sample characteristics are listed in Table 1. Glass transition temperatures T_g were measured with a Perkin–Elmer DSC-4 calorimeter. Each sample was previously submitted to the same thermal history consisting of heating the sample from 50 to 280 °C at heating rate $\beta = 20\,°\mathrm{C\ min}^{-1}$, and keeping it at 280 °C the required time (about 30 min) in order to remove memory effects. After that, cooling in the quickest manner possible took place, and during the next heating process at the desired β, the corresponding thermogram was registered.

For each sample, the T_g value increased slightly with heating rate and decreased with molecular weight, if the experiments were performed at the same β. Extrapolating the T_g values to $\beta = 0$, the resulting T_g^0 values were independent of molecular weight. On the other hand, T_g depends on β in a linear form (see Fig. 1). The variation of T_g with molecular weight was demonstrated by applying the Fox–Flory relationship. Figure 2 shows a straight line for each heating rate and Fig. 3 is a plot of T_g^{∞} and K values against β, exhibiting the following dependences

$$T_g^{\infty} = 516 + 0.143\beta$$

$$K = 3.421 + 0.0027\beta$$

When these results are compared with those for monodisperse poly(*N*-vinylcarbazole) (PNVC) samples, obtained by fractionation from cationic-synthesized polymer and submitted to the same thermal history as above [4],

TABLE 1

Characteristics of poly(3-Br-*N*-vinylcarbazole) samples

Fraction	$\overline{Mn}$ ($\times 10^{-5}$)	$\overline{Mw}/\overline{Mn}$	$[\eta]$ [a]
F-1	2.8	1.24	0.446
F-2	1.6	1.20	0.312
F-3	1.0	1.13	0.230
F-4	0.5	1.19	0.154

[a] $[\eta]$ is the intrinsic viscosity in tetrahydrofuran at 25 °C.

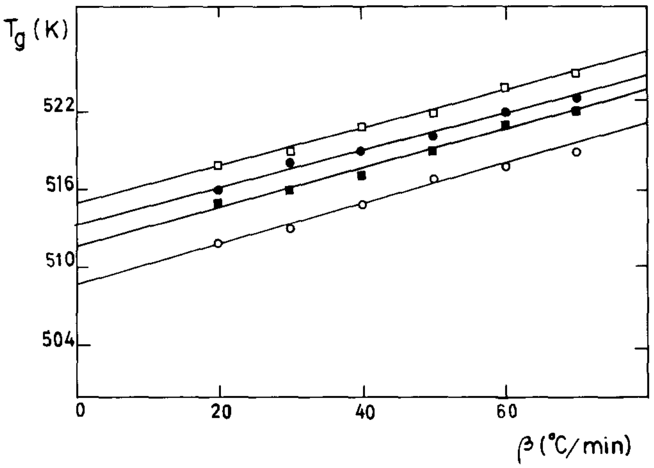

Fig. 1. Glass transition temperature T_g versus heating rate β for PBrNVC samples.

it was observed that the T_g^∞ values for PNVC are lower than those for PBrNVC and, moreover, its variation with β is also lower. However, for PBrNVC samples, the K values are very close when β varies; while for PNVC samples, K clearly varies with β (see Fig. 4).

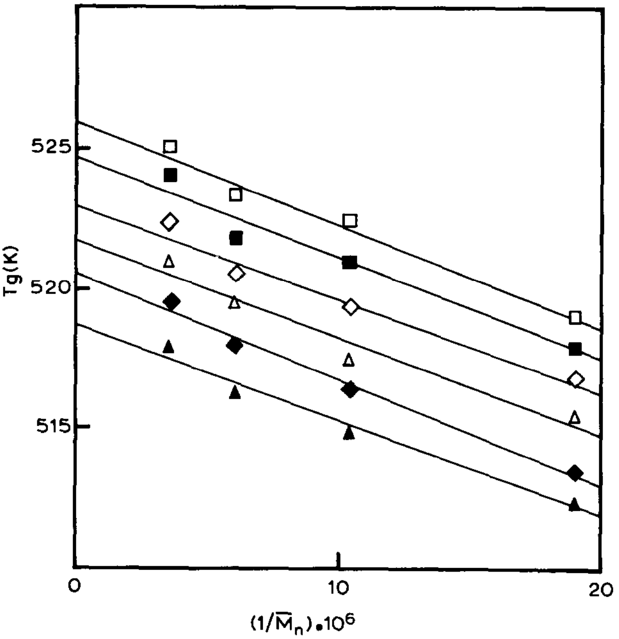

Fig. 2. T_g values versus $1/\overline{Mn}$ for PBrNVC samples at: ▲, 20 °C $\min^{-1}$; ◆, 30 °C $\min^{-1}$; △, 40 °C $\min^{-1}$; ◇, 50 °C $\min^{-1}$; ■, 60 °C $\min^{-1}$; and □, 70 °C $\min^{-1}$.

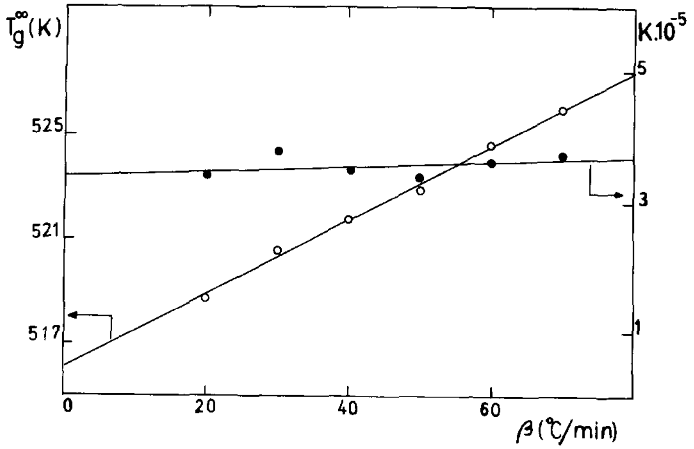

Fig. 3. T_g^∞ and K values versus β for PBrNVC.

The activation energy conferred to the glass transition process has been calculated from the established equation given by Kissinger [5], assuming that a first-order kinetic process took place

$$\ln\left(\beta/T_g^2\right) = C - E/RT_g \tag{2}$$

where R is the gas constant, E is the activation energy and C is a constant. Both E and C depend on the polymer. By plotting $\ln(\beta/T_g^2)$ against $1/T_g$ for each molecular weight, the corresponding E values were obtained and they are listed in Table 2. The E values are grouped around an average value, 382 kJ mol^{-1}, which appears to be independent of the macromolecular size and represents the energy required for one representative segment of the chain to be moved from one side to another vacant side.

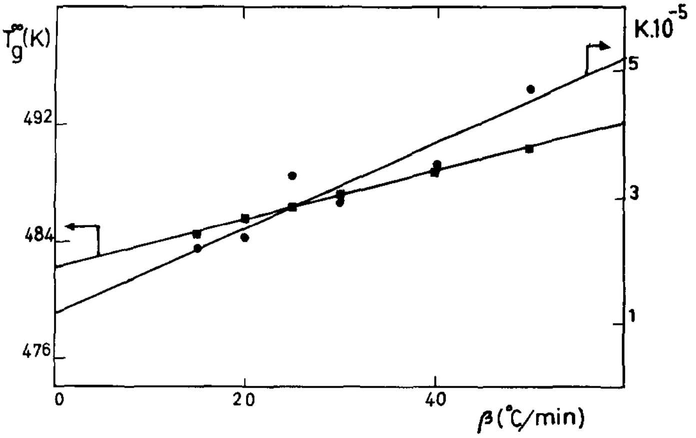

Fig. 4. T_g^∞ and K values versus β for PNVC.

TABLE 2

T_g (K) values of poly(3-Br-*N*-vinylcarbazole) at different heating rates, β, and the energy value, E, for each sample

Fraction	β (°C min^{-1})							E (kJ mol^{-1})
	0	20	30	40	50	60	70	
F-1	515	518	519	521	522	524	525	377
F-2	514	516	518	519	520	522	523	397
F-3	512	515	516	517	519	521	522	349
F-4	509	512	513	515	517	518	519	404

Cationic PNVC samples showed a syndiotacticity X_s of around 0.56, measured by Terrell's procedure [6] (Table 3) and the average E value, 431 kJ mol^{-1} was 13% larger than for PBrNVC, in spite of PNVC having the lower T_g. The PBrNVC chain is more flexible because the syndiotactic stereoblocks result in the transition process in cationic PNVC requiring more energy. From ref. 7, the activation energy for PNVC of radical origin is 323 kJ mol^{-1} which is 33% lower than that for cationic PNVC and even 18% lower than that for PBrNVC, indicating that Br atoms remove flexibility from the PNVC chain.

So, in order to improve rigidity, halogen atoms must be added to the carbazoyl group before radical or cationic polymerization, depending on the degree of rigidity required. Bearing in mind eqn. (1) and the variations of K and T_g^∞ with β (Figs. 3 and 4), it seems that rigidity effects caused by Br atoms or stereoblocks have more effect on the T_g^∞ term because this modifies the T_g values; furthermore, the K term is divided by $\overline{Mn}$. The chain becomes more rigid as the variation of T_g^∞ with β decreases.

TABLE 3

Characteristics of cationic poly(*N*-vinylcarbazole) samples

Fraction	$\overline{Mn}$ ($\times 10^{-5}$)	$\overline{Mw}/\overline{Mn}$	x_s [a]
P-1	10.6	1.36	0.56
P-2	10.2	1.53	0.56
P-3	5.7	1.93	0.56
P-4	6.1	1.21	0.56
P-5	2.7	1.53	0.56
P-6	2.4	1.44	0.56

[a] X_s is the syndiotactic diad mole fraction [6].

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