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Synthesis and Characterization of the *N*-Vinylcarbazole–Methyl Methacrylate and *N*-Vinylcarbazole–Methyl Acrylate Copolymer Systems. Thermogravimetric Study

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ABSTRACT: Copolymerization of *N*-vinylcarbazole with methyl methacrylate and methyl acrylate has been studied obtaining the reactivity ratios for both systems in tetrahydrofuran. A thermal study of the copolymers related to the *N*-vinylcarbazole content has been carried out taking into account several theories predicting the dependence of the glass transition temperature on the copolymer composition.

KEY WORDS Copolymer / Glass Transition Temperature / Thermal Stability /

Poly(*N*-vinylcarbazole) (PNVC), is a very interesting polymer due to its electrical and photoconductive properties.[1-3] However, it has a high glass transition temperature ($T_g \approx 490$ K). The glass transition is of special importance in polymer field as it reflects the flexibility of the polymer chain and therefore, it limits the possible applications of the material. The high T_g of PNVC makes necessary the use of high processing temperatures which often cause polymer degradation. Low T_g polymeric materials could be synthetized by using comonomers of relatively low T_g. These copolymers would be able to maintain some of the PNVC relevant properties specially if they are doped with small electron-acceptor molecules as reported by other authors.[2-4]

The main of this paper concentrates on the study of thermal properties of copolymers. Copolymerization of *N*-vinylcarbazole (NVC) with methyl methacrylate (MMA) and with methyl acrylate (MA) has been carried out, where the homopolymers T_g reached values of 391 K and 262 K, respectively. The copolymerization process has been studied for both systems and the T_g experimental values of all the synthetized samples have been measured. The prediction of the variation of T_g with the copolymer composition has been attempted by several authors[5-7] and some of these models have been applied to our systems. Moreover, the possible practical applications of these materials are directly related to their thermal stability and so, this paper also focuses on the study of the thermal degradation of these copolymers as a function of their composition.

EXPERIMENTAL

NVC (Fluka) prior to dry in a vacuum line and store in the dark, it was recrystallized several times from hot methanol under dry nitrogen.

MMA, and MA (Fluka) were dried over calcium hydride and fractionally distilled under vacuum.

α,α'-Azobisisobutyronitrile (AIBN) (Fluka) was recrystallized from diethyl ether.

Methanol (Scharlau) and tetrahydrofuran (THF) (Scharlau) were purified by standard procedures.

The copolymerization study was extended to cover all the range of monomer feed compositions. The copolymerization reactions were carried out using THF as solvent and AIBN as initiator which concentration was 0.1% by mole in relation to the total monomer. The desired amount of the required reagents was added to the reaction flask which was evacuated by several freeze-thaw cycles and then, sealed under vacuum and placed in a thermostatic bath at 323 K.

The copolymer was isolated by precipitation into methanol and then reprecipitated from a THF solution into an excess of hot methanol. Finally, the copolymer was dried in a vacuum line at room temperature for 48 h.

The amount of nitrogen contained in the copolymers was determined by elemental analysis and from it, the copolymer composition was obtained. A Perkin Elmer Elemental Analyzer CHN 2400 was used.

The molecular weight of the copolymers (referred to polystyrene equivalents) was obtained by gel permeation chromatography (GPC) using a Waters Chromatograph with THF as solvent at 298 K. Two Shodex columns with an exclusion limit of 5×10^7 were used. A previous calibration with standard polystyrene samples was performed.

The glass transition temperature measurements were carried out in a Perkin Elmer DSC-4 Calorimeter with a heating rate of 20°C min^{-1}.

Thermogravimetric degradations were measured using a Perkin Elmer TGS-2 Thermobalance. A standard dynamic heating procedure was followed from room temperature to 873 K (heating rate $= 10$°C min^{-1}). Samples of 6—7 mg and a stream of dry nitrogen were used.

RESULTS AND DISCUSSION

The reaction conditions, monomer feed, copolymer composition, molecular weight, polydispersity (I), and T_g values are fully detailed on Tables I and II. The Figure 1 shows the relationship between the mole fraction of NVC in the copolymer (F_1) and the mole fraction in the monomer feed (f_1) for both systems.

Analysis of the experimental monomer feed ratios

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Table I. Copolymerization of NVC with MMA and copolymer characteristics

Sample	Monomer feed mol% NVC	Polym. time min	Conv. wt%	Copolymer comp. mol% NVC	$M_n \times 10^{-4}$ $\mathrm{g\,mol^{-1}}$	I	T_g K
PMMA	0	480	12.1	0	32.4	1.53	391
MMANVC7	10	420	13.3	4.08	17.5	1.61	402
MMANVC8	20	360	15.3	8.31	17.6	2.06	408
MMANVC5	35	330	8.23	14.4	21.9	1.58	—
MMANVC1	50	320	7.41	23.0	28.2	1.83	419
MMANVC6	65	300	14.8	31.6	24.3	1.95	—
MMANVC3	80	180	8.60	40.8	17.4	2.22	442
MMANVC4	90	118	11.4	53.5	28.0	1.79	450
PNVC	100	150	15.2	100	1.80	1.59	486

Table II. Copolymerization of NVC with MA and copolymer characteristics

Sample name	Monomer feed mol% NVC	Polym. time min	Conv. wt%	Copolymer comp. mol% NVC	$M_n \times 10^{-3}$ $\mathrm{g\,mol^{-1}}$	I	T_g K
PMA	0	300	12.3	0	—	—	262
MANVC4	10	60	16.5	11.1	44.4	1.61	292
MANVC2	20	72	18.7	20.0	45.9	1.86	295
MANVC5	40	60	21.4	31.6	33.2	1.67	365
MANVC1	50	60	13.6	36.0	27.8	1.60	348
MANVC7	70	64	22.7	44.3	29.1	1.66	370
MANVC3	80	65	14.3	48.4	66.0	1.82	386
MANVC6	90	60	13.4	57.8	60.5	1.50	418
PNVC	100	150	15.2	100	18.0	1.59	486

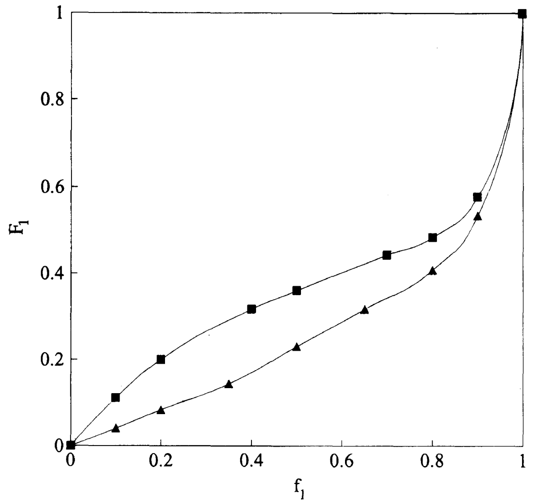

Figure 1. Copolymerization diagrams of NVC–MMA (▲) and NVC–MA (■) systems.

together with the copolymer compositions allow the calculation of the reactivity ratios for each pair of monomers. Due to the absence of charge transfer complexes in these systems, the reactivity ratios have been calculated assuming that the terminal model for free radical copolymerization proposed by Mayo and Lewis[8] is applicable to the data under consideration. This model postulates that the addition rate of a monomer to a growing polymer chain is independent of the chain length and depends only on the nature of the terminal radical unit. The copolymer composition equation for this model is:

$$F_1=\frac{r_1 f_1^2+f_1 f_2}{r_1 f_1^2+2 f_1 f_2+r_2 f_2^2} \tag{1}$$

where f_1 and f_2 are, respectively, the mole fraction of monomer M_1 and M_2 in the feed, F_1 is the mole fraction of M_1 in the copolymer, r_1 and r_2 are the monomer reactivity ratios.

The calculation of r_1 and r_2 requires firstly to accomplish several copolymerization reactions at low conversions with different monomeric compositions in the feed, and secondly, the analysis of the monomeric composition in the copolymer.

Several methods[9,10] can be used to linearize the composition equation. Taking into account that proposed by Kelen and Tüdos,[10] the copolymer composition equation can be rearranged by defining the variables:

$$G=\frac{f_1}{f_2}\left[\frac{F_1-F_2}{F_1}\right] \quad \text{and} \quad F=\left[\frac{f_1}{f_2}\right]^2\frac{F_2}{F_1} \tag{2}$$

So the eq 1 can be written as follows:

$$\frac{G}{\alpha+F}=\left(r_1+\frac{r_2}{\alpha}\right)\frac{F}{\alpha+F}-\frac{r_2}{\alpha} \tag{3}$$

Where α denotes an arbitrary constant ($\alpha>0$) given by:

$$\alpha=\sqrt{F_{\mathrm{MAX}}\cdot F_{\mathrm{MIN}}} \tag{4}$$

Being F_{MAX} and F_{MIN} the maximum and minimum values of F, respectively.

By introducing:

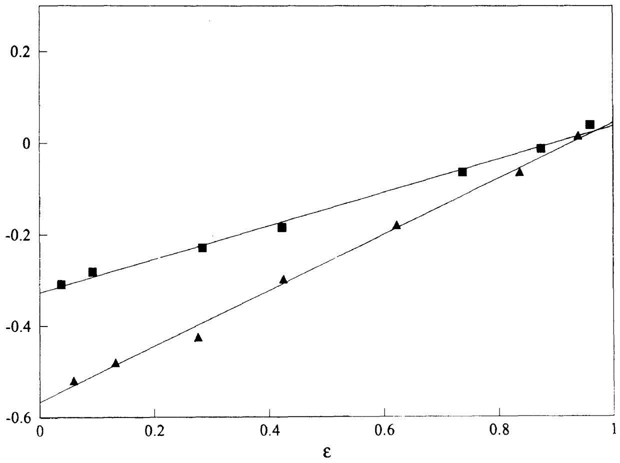

Figure 2. Kelen–Tüdos plots for NVC–MMA (▲) and NVC–MA (■) systems.

$$\eta=\frac{G}{\alpha+F} \quad \text{and} \quad \varepsilon=\frac{F}{\alpha+F} \tag{5}$$

the eq 3 transforms into:

$$\eta=\left(r_1+\frac{r_2}{\alpha}\right)\varepsilon-\frac{r_2}{\alpha} \tag{6}$$

which allows the calculation of the reactivity ratios from the copolymers composition data. Figure 2 shows the straight lines obtained for the two systems and their respective r_1 and r_2 values are:

NVC–MMA copolymer	NVC–MA copolymer
$r_1 = 0.045$	$r_1 = 0.037$
$r_2 = 2.56$	$r_2 = 0.79$
$r_1r_2 = 0.114$	$r_1r_2 = 0.029$

These values suggest that the copolymers have an alternating character. The reactivity ratios obtained for the NVC–MMA system are in agreement with those reported by Curteanu *et al.*[11] using benzene as solvent at 343 K, and those recalculated by this author from previous data found for this system.[12–14]

Glass Transition Temperature

Effect of the Copolymer Composition. The glass transition temperatures for both systems are shown on Tables I and II. Despite the great difference observed between r_1 and r_2 in both systems, there is no microphase separation in the bulk state because all the samples show a single glass transition at the temperature range given by the T_g of the respective homopolymers. As it can be seen, the higher the NVC content in the copolymer, the higher the T_g. The possible prediction of the glass transition temperatures as a function of the copolymer composition has been considered by the application of several theories.

Fox[5] first proposed an additive relation:

$$\frac{1}{T_g}=\frac{w_1}{T_{g1}}+\frac{w_2}{T_{g2}} \tag{7}$$

where w_1 and w_2 are the NVC and the respective comonomer weight fractions in the copolymer; T_{g1} and T_{g2} are the glass transition temperatures of the respective homopolymers. The application of the eq 7 for both systems is shown in Figure 3.

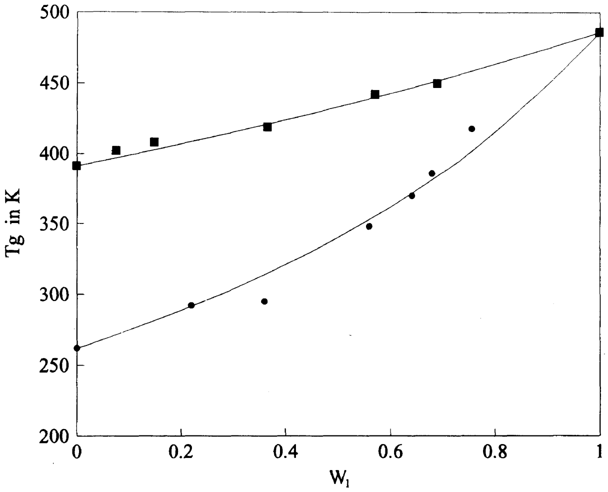

Figure 3. T_g values *versus* copolymer composition for NVC–MMA (■) and NVC–MA (●) systems. The solid lines represent the values calculated by the Fox equation.

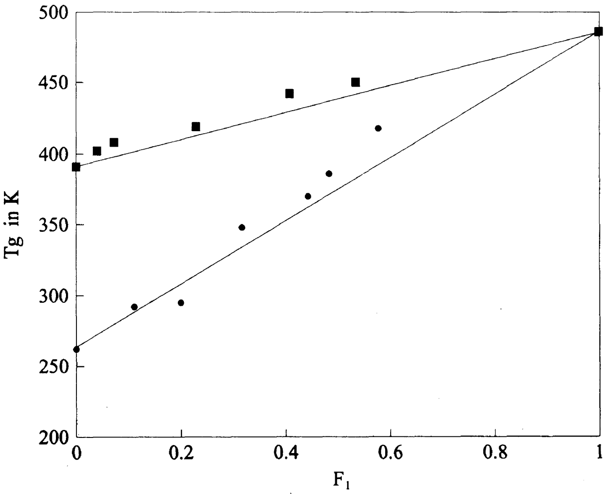

Figure 4. Application of the Di Marzio–Gibbs equation for predicting T_g in function of the copolymer composition; (■): NVC–MMA, experimental values; (●): NVC–MA, experimental values.

Di Marzio and Gibbs[6] proposed a simple relation which describes a linear behavior of T_g with copolymer composition:

$$T_g=F_1T_{g1}+F_2T_{g2} \tag{8}$$

where F_1(NVC) and F_2(MA, MMA) are mole fractions in the copolymer. The application of eq 8 for our systems is shown in Figure 4.

These theories however, do not take into account the interactions given by the presence of two different monomeric units. In general, it would be expected that the different nature of the comonomers would generate steric and energetic effects when are linked together. Furthermore, the heterolinkages would give different contribution to the rotational barrier and free volume than those of the respective homopolymers. In this sense, there are other theories that also consider the sequence distribution in the copolymer. One example is the model proposed by Johnston,[7] derived from the Fox theory, which assumes that diads formed by equal monomeric

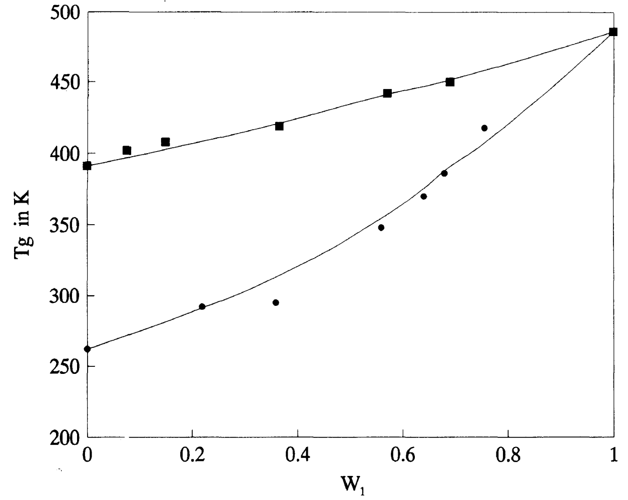

Figure 5. Plot of the glass transition temperatures in function of the copolymers composition according the Johnston theory: (■): NVC–MMA, experimental values; (●): NVC–MA, experimental values.

units 1–1 or 2–2 have the same interactions as those seen in the respective homopolymers. However, the presence of heterodiads will cause new interactions which could modificate the 1 or 2 monomeric unit contribution to the T_g value. Thus, to predict the T_g more accurately, it is necessary to assign their own T_g values for heterodiads. Assuming that 1–2 and 2–1 sequences have the same T_g, the following equation can be obtained:

$$\frac{1}{T_g}=\frac{P_{11}w_1}{T_{g11}}+\frac{P_{22}w_2}{T_{g22}}+\frac{P_{12}w_1+P_{21}w_2}{T_{g12}} \qquad (9)$$

where T_{g11}(PNVC) and T_{g22}(PMA, PMMA) refer to the homopolymers and T_{g12} corresponds to the 1–2, 2–1 diads. P_{ij} is the probability for *ij* linkages in the chain which can be calculated from the reactivity ratios[15]:

$$P_{ij}=\frac{1}{1+r_i\dfrac{[i]}{[j]}} \qquad (10)$$

$$P_{ii}=1-P_{ij} \qquad (11)$$

where $[i]$ and $[j]$ are the concentrations of each monomer in the feed.

To apply this theory it is necessary to assign a value to T_{g12}. These values have been obtained from the experimental data of the T_{g11}, T_{g22} and the copolymers T_g prepared at low conversions, using the linearized expression of eq 9. The values were:

NVC–MMA system: $T_{g12}=449.6\,\mathrm{K}$

NVC–MA system: $T_{g12}=383.3\,\mathrm{K}$

Figure 5 shows the theoretical dependence of T_g on copolymer composition according to this theory as well as the experimental results obtained. It is observed that in both systems the T_{g12} is slightly higher that the mean of the respectively homopolymers glass transition temperatures. This fact would indicate the presence of a positive deviation from the ideal behavior. According to this, weak attractive interactions between comonomers could be expected. Taking into account the electron-donor behavior of the PNVC, these interactions could be generated by electrostatic forces between NVC and the respective comonomer. This is more probable in the case of the MA which has a stronger electron-acceptor character than the MMA.

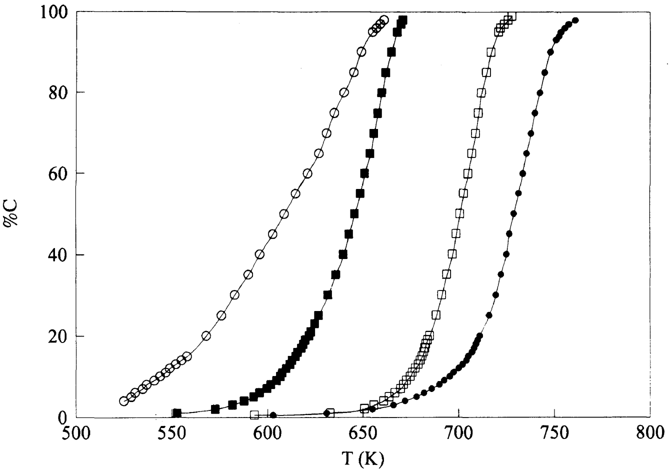

Figure 6. Degradation curves for NVC–MMA system (○, PMMA; ■, MMANVC7; □, MMANVC3; ●, PNVC).

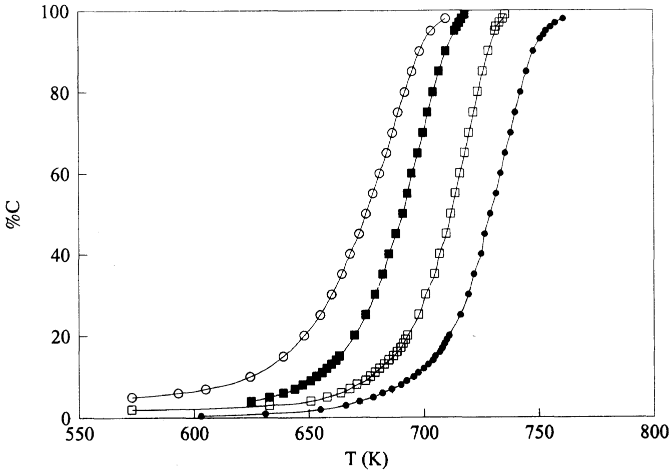

Figure 7. Degradation curves for NVC–MA system (○, PMA; ■, MANVC4; □, MANVC7; ●, PNVC).

As it can be observed the behavior of the NVC–MMA system can be predicted adequately by both the Fox and Johnston's theories. It seems that the consideration of the sequence distribution in the copolymer does not improve the results obtained by the application of the Fox's theory. Only weak interactions will exist between both monomers and as both monomers are bulky, the difference between the rotational barrier associated to the heterolinkages or homolinkages could not have a great influence. In relation to the NVC–MA system, neither of these theories agree with the experimental behavior. Both homopolymers have very different T_g values (above 200 K) and therefore, different chain flexibility. It is probable that as the interactions are not so weak, a more accurate consideration of the heterolinkages contribution could be necessary in order to obtain a better theoretical approximation to the experimental behavior.

Thermal stability

Figures 6 and 7 show the degradation thermograms

Table III. Degradation of NVC–MMA copolymers (heating rate = 10°C min^{-1})

Sample	Copolymer comp. mol% NVC	T_i K	E_a kJ mol^{-1}
PMMA	0	585	75.42
MMANVC7	4.08	621	137.5
MMANVC3	40.8	681	235.8
MMANVC4	53.5	697	253.3
PNVC	100	707	256.7

Table IV. Degradation of NVC–MA copolymers (heating rate = 10°C min^{-1})

Sample name	Copolymer comp. mol% NVC	T_i K	E_a kJ mol^{-1}
PMA	0	635	152.5
MANVC4	11.1	669	175.0
MANVC1	36.0	694	127.5
MANVC7	44.3	701	235.8
MANVC6	57.8	699	245.4
PNVC	100	707	256.7

for two copolymers and the respective homopolymers at a heating rate of 10°C min^{-1}. The percent mass loss is plotted as a function of temperature where the 100% mass loss is attained in all cases.

The thermal stability is measured by the onset decomposition temperature, T_i, which is calculated as the intersection of the initial baseline with the experimental curve. The obtained values for our systems are shown on Tables III and IV. The hindered interaction of the bulky carbazole group with the main chain makes the thermal stability of PNVC higher than that observed for PMMA or PMA. Furthermore, the both copolymer systems have a high thermal stability which is close to that observed for the PNVC homopolymer at a 50% by mole of NVC. The activation energy of the degradation process (Tables III and IV) has been obtained for each sample by the McCallum and Tanner's[16] method. The obtained values for both systems corroborate the high thermal stability observed for the copolymers which increases with increasing the NVC content.

It can be concluded that the introduction of MMA or MA units in the PNVC chain involves a decrease in the glass transition temperature of the system. This fact could facilitate their industrial processing with a relatively small decrease in the thermal stability.

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