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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Rytzel, Anna(1997) 'Thermomechanical and Dielectrical Properties of Alkyl Methacrylate with N-Vinyl Carbazole Copolymers', Journal of Macromolecular Science, Part A, 34: 1, 211 – 219

To link to this Article: DOI: 10.1080/10601329708014948

URL: <http://dx.doi.org/10.1080/10601329708014948>

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THERMOMECHANICAL AND DIELECTRICAL PROPERTIES OF ALKYL METHACRYLATE WITH N-VINYL CARBAZOLE COPOLYMERS

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ABSTRACT

Copolymers of methyl methacrylate and ethyl methacrylate with N-vinyl carbazole were synthesized by free-radical bulk polymerization using benzoyl peroxide as an initiator. The thermal stability, glass transition temperature, Brinell hardness and dielectric properties at different temperatures, were studied. The effect of N-vinyl carbazole content on the properties of copolymers is discussed.

INTRODUCTION

Poor thermal stability, hardness or chemical resistance of methacrylate polymers are well known. Many investigations have been conducted to obtain copolymers with this property improved [1-7]. On the other hand, good thermal stability and high dielectric constant of N-vinyl

carbazole polymers [8,9], seem promising and can be used to modify alkyl methacrylates by copolymerization with N-vinyl carbazole monomer.

This paper presents further results on the free-radical bulk copolymers of methyl methacrylate with N-vinyl carbazole (MeMA/N-VC) and ethyl methacrylate with N-vinyl carbazole (EtMA/N-VC) as well as some of their properties, especially electrical ones. The copolymers were obtained by free-radical bulk polymerization with benzoyl peroxide as an initiator. Each copolymer contained 5, 10, 15 and 20 wt.% of N-vinyl carbazole units. The contents of copolymers was checked by elemental and IR analysis.

MATERIALS

Methyl methacrylate (MeMA), pure (Chemical Works, Oświęcim, Poland), was purified by repeated several times extraction with 5% NaOH and 20% NaCl solution, dried over anhydrous magnesium sulphate and then distilled under reduced pressure just before used. $n_D^{20} = 1.4145$, $d_4^{20} = 0.9424 \text{ g}\cdot\text{cm}^{-3}$.

Ethyl methacrylate (EtMA), pure (Fluka, A.G., Switzerland). The monomer was purified in the same manner as methyl methacrylate. $n_D^{20} = 1.4135$, $d_4^{20} = 0.9127 \text{ g}\cdot\text{cm}^{-3}$.

N-Vinyl carbazole (N-VC), pure (Fluka AG, Switzerland). The monomer was purified by recrystallization from acetone. M.p. = 336.5 to 338K. The content of nitrogen determined by Kiejdahl method was 13.49% (calculated 13.5092%).

Benzoyl peroxide (BP), pure grade (Argon, Łódź, Poland), containing 86.5 % of assay [10] was used as supplied.

METHODS

The copolymers of MeMA/N-VC and EtMA/N-VC were obtained by free radical copolymerization using 0.3 wt% BP as the initiator. Under the same conditions homopolymers of methacrylates were obtained for reference. The bulk copolymerization was carried out in glass tubes, which were heated in a water thermostat and held at different

Table 1. Composition of AMA/N-VC copolymers

Sample No	AMA wt. %	N-VC wt. %	N-VC copolymers wt. %*	
			MeMA	EtMA
I	95	5	4.61	4.85
II	90	10	11.5	10.8
III	85	15	14.9	16.4
IV	80	20	24.1	23.7
V	100	-	-	-

* -Calculated from elemental analysis

temperatures and times as described previously [6]. The nominal content of N-VC in each copolymer was about 5, 10, 15 or 20 wt.%. Compositions of copolymers are presented in Table 1.

MEASUREMENTS

Thermal studies were carried out using the OD -102 derivatograph (Hungary) in an oxidizing (air) atmosphere with 200 mg of the powdered to 1273 K at a constant heating rate 283 K/min. The sensitivity of the instrument was 1/20 for DTA and 1/10 for DTG. Additional thermal studies were carried out by the Madorsky method [11]. The measurements were made in the temperature range 373 to 673 K in air atmosphere.

The measurements of the softening point were carried out in a Vicat apparatus (Rσ Caest Torino, Italy). The samples were in the form of discs of ca. 30 mm diameter and ca. 5 mm thickness. The load was 49 N at heating rate of 323 K/h.

The T_g measurements of the copolymers were carried out using Höppler consistometer (VEB Prüfgeräte-Werk, Medingen, Type 0481, Germany). The load was 0.5 kg.

The hardness was measured by Brinell tester (HPK 746, Feinmechanic, Ralf Kögel, Germany). The hardness was calculated from the formula: $H_K = F/d \cdot \pi \cdot h$ (in kg/cm^2), where F is load in kg, d is the diameter of the probe ball in cm, and h is the depth of cavity in cm.

The dielectric constant ϵ was measured for the samples in form of discs ca. 30 mm diameter, and ca. 0.9 -1.5 mm tickness. The samples were covered by transmsion paint, which played a part of capacitors. The measurements of the capacity were taken in temperature range from 293 to 353 K. The dielectric constant ϵ was calculated from the formula: $\epsilon = d \cdot c / \epsilon_0 \cdot s$, where d isthe tickness of disc in mm, c is the capacity of a capacitors, $\epsilon_0 = 8.8541 \cdot 10^{-12}$ (constant), and s is the surface of the samples.

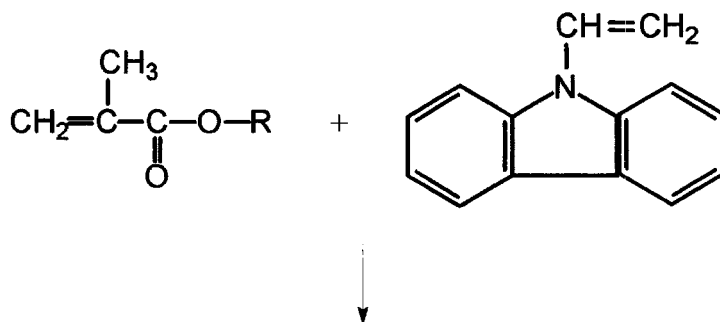
IR spectra of copolymers (KBr pellets) were recorded on a SPECORD-71 IR spectrometer (Carl Zeiss Jena, Germany).

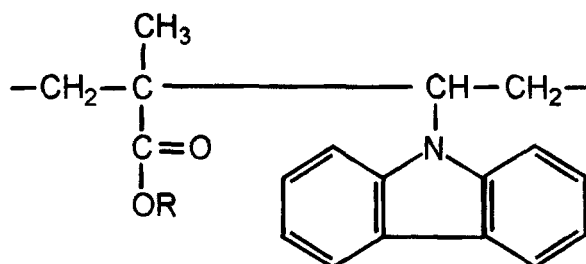
The elemental analysis was carried out using EA 1108 Elemental Analyzer (Carlo Erba, Italy).

RESULTS AND DISCUSSION

The copolymers MeMA/N-VC, EtMA/N-VC and poly(alkyl methacrylates) were obtained by free-radical bulk polymerization using 0.3 wt.% of BP as an initiator.

The simplified reaction scheme of the copolymerization is the following:





where: R = -CH₃, -C₂H₅

The polymerization was carried out sufficiently long and at such a temperature regime that practically all the comonomers converted into polymer. The copolymerization process was described in details previously [6]. The compositions of the polymerization mixture and compositions of copolymers calculated from elemental analysis are reported in Table 1.

The thermal stability of homo- and copolymers was examined by the static (Madorsky's) and dynamic methods of thermal analysis, as well as by determination of the Vicat softening points. The glass transition temperature (T_g), and Brinnell hardness was examined, too.

By Madorsky's method [11], two series of measurements were carried out for powdered homo- and copolymers of different compositions. The thermal stability temperature was taken to be the temperature of 50% weight loss of the sample (T_{d50}). The thermal stability of homo- and copolymers was also examined by a dynamic method by using derivatograph. From DTG the thermal stability was read out as the temperature of the maximum decomposition rate (T_{max}). The T_{d50} and T_{max} data for the homo- and copolymers are summarized in Tables 2 and 3. The values of T_{d50} and T_{max} varied with the copolymer composition. For the homopolymers, both values of T_{d50} and T_{max} were the smallest, while an increase of N-VC content in the copolymer caused a rise of these values. The thermal stability of EtMA/N-VC systems was smaller than that of MeMA/N-VC copolymers. Both values of T_{d50} and T_{max} were smaller by ca. 10K.

Finally, the thermal stability of the copolymers was examined by measuring the Vicat softening point. The data in Tables 2 and 3 show that the softening points of the copolymers depends on N-VC contents. It has

Table 2. Properties of MeMA/N-VC copolymers

Copoly -mer No	MeMA/N-VC				
	T _{d50} [K]	T _{max} [K]	Vicat [K]	T _g [K]	Brinell hardness kg/cm ²
I	528	613	374	247	1148.7
II	536	619	377	253	1172.6
III	545	624	382	258	1236.0
IV	557	631	385	263	1262.6
V	519	603	372	-	1069.3

Table 3. Properties of EtMA/N-VC copolymers

Copoly -mer No	EtMA/N-VC				
	T _{d50} [K]	T _{max} [K]	Vicat [K]	T _g [K]	Brinell hardness kg/cm ²
I	514	602	347	245	850
II	532	611	337	249	863
III	541	614	354	253	883
IV	548	619	358	258	904.7
V	503	593	338	-	710

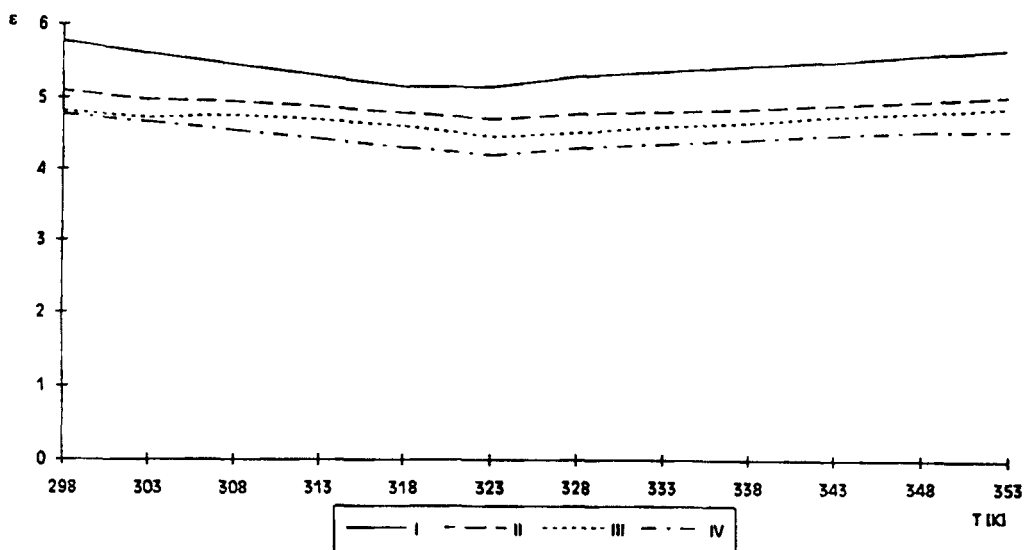


Fig.1. The temperature dependence of dielectric constant ϵ for MeMA/N-NVC copolymers. The curve labels correspond to sample numbers in Table 1

been established that with the increase of N-VC content, the softening point increases, but the differences are rather small.

The glass transition temperature (T_g), and Brinell hardness are also shown in Tables 2 and 3. The T_g values increased slightly as N-VC content in the copolymer increased. The T_g 's of MeMA/N-VC copolymers are noticeable higher than those of EtMA/N-VC once.

The Brinell hardness also shows a tendency to increase with N-VC content. The MeMA/N-VC systems have significantly higher hardness than EtMA/N-VC copolymers.

The dielectric properties of copolymers were studied as a dependence of dielectric constant against temperature. The samples were in the form of discs of ca. 30 mm diameter. Covered by a transmission paint, the discs played a part of capacitors. The measurements of the capacity were taken in temperature range 293-353 K.

The dependences $\epsilon = f(T)$ [K] are plotted in Figures 1 and 2. All the copolymers showed two jumps in dielectric constant (ϵ). In the

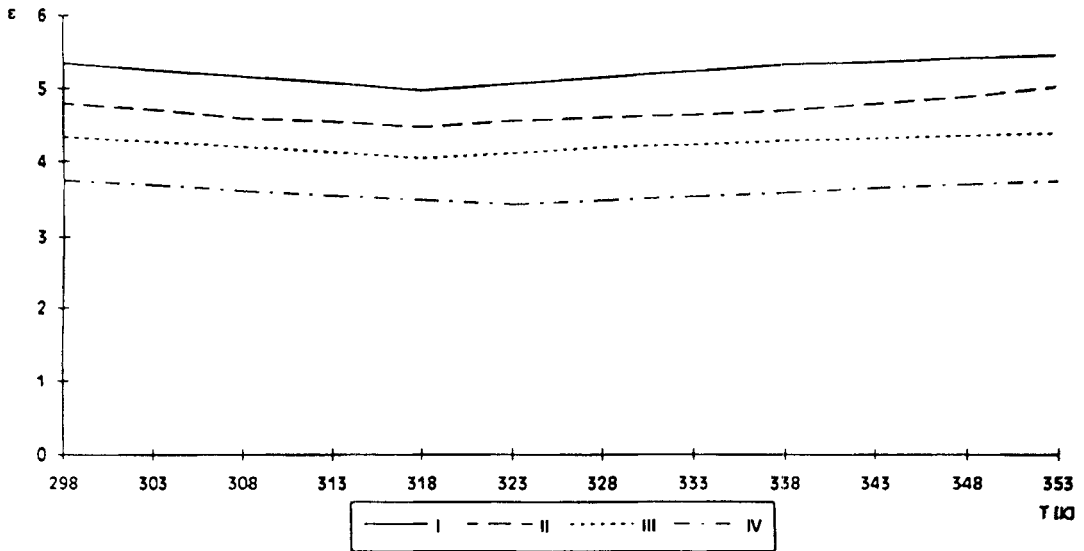


Fig.2. The temperature dependence of dielectric constant ϵ for EtMA/N-VC copolymers. The curve labels correspond to sample numbers in Table 1.

temperature range from 293 to 323 K the value of dielectric constant (ϵ) was roughly inversely proportional to temperature, and then the temperature range from 323 to 353 K, the value of ϵ was directly proportional to temperature. The content of N-VC in copolymers effected the dielectric constant, too. A significant decrease of ϵ values with increasing content of N-VC in copolymers was observed. The dielectric constant for EtMA/N-VC systems were slightly smaller compared to those for MeMA/N-VC copolymers.

CONCLUSION

In the copolymerization of MeMA and EtMA with N-VC, the copolymers differing in composition were obtained. Generally, it has been found that with an increase of N-VC content in the copolymers, their thermal stability increases. This confirms the expected thermal stabilizing influence of N-VC. The dielectric constant (ϵ) changed with temperature

with two steps. In the first step in temperature range from 293 to 323 K the ϵ value was inversely proportional to temperature, while in the second, at 323 to 353 K, the ϵ value was directly proportional to temperature.

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