

Grafting N-vinyl-carbazole on alternating copolymers obtained from dicyclopentadiene

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Copolymers based on dicyclopentadiene and maleic anhydride have been grafted with poly-vinylcarbazole chains using the ATRP technique. We have found the appropriate conditions for performing the grafting, and the resulting conversions have been established. All grafted copolymers have been characterized from the structural point of view, as well as by measuring their improved thermal properties.

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1. Introduction

It has been proven that dicyclopentadiene (DCPD) cannot homopolymerize through a radical mechanism; however, its quasi-alternating copolymers with maleic anhydride (MA) have been briefly described by Gaylord [1], and subsequently by Rzaeva and co-workers [2]. In our works we have reported detailed kinetic investigations that, in turn, have depicted specific features of the copolymerization process [3-6]. Nevertheless, the binary (quasi-alternating copolymers) with the ternary copolymers exhibit low molecular weights; this fact influences their low thermal resistance.

In order to increase the usefulness of the products, we have grafted N-vinyl carbazole (NVKZ) chains, known for their stiffness. The chosen method was ATRP technique [7-8] as a mild synthetic reaction. This method has been already used [9-10] for poly-(NVKZ), but not on the present substrate.

2. Experimental

2.1 Materials

MA (Merck) was purified by recrystallization from chloroform, while DCPD (Aldrich) has been used as such; indene (IN) (Fluka) was submitted to distillation (p=5 mmHg, T=44.3°C).

Initiator, namely lauroyl peroxide (LP), (Merck) as well as NVKZ (Fluka) were purified by recrystallization from ethanol (anhydrous, Aldrich) or methanol, respectively.

Solvents and non-solvents, namely dimethyl-formamide (DMF), anisole (ANI), ethyl ether (ET) or tetra-hydro-furan (THF) have been purified by distillation. Bromine (Aldrich) has been used as such. Copper chloride (CuCl - Fluka), employed as co-initiator

was carefully washed with acetic acid, until the total disappearance of the green color in the effluent.

2,2'-bi-pyridyl (Byp) (Merck) has been used as complexing agent; anisole (ANI - Fluka) was employed as specific solvent in halogen-transfer polymerizations (ATRP).

2.2 Syntheses for support-polymers

Binary copolymer MA-DCPD has been prepared as previously reported [3-5]; the synthesis started from an equimolecular monomer mixture ($[M_{01}] + [M_{02}] = 3.5$ mole/l), $LP = 5 \times 10^{-2}$ mole/l in DMF. The reaction has been carried out at 80°C under a nitrogen cushion; after 3 hours, the resulted copolymer has been separated by precipitation in ET, and subsequently filtered and dried.

The ternary copolymer MA-DCPD-IN was synthesized in homogeneous solution (DMF) starting from the following monomer feed composition: $[AM] = 1.75$ mole/l, $[DCPD] = 0.875$ mole/l; $[IN] = 0.875$ mole/l. Carrying out the copolymerization at 80°C initiated by LP (5×10^{-2} mol/l) we have found a quasi-total conversion after 3 hours; the ternary copolymer was separated after precipitation in ET, followed by filtration, drying and weighting.

Brominating the binary (or ternary) copolymer: A polymer solution (10%) in DMF has been introduced into a vial together with Br_2 in excess (with respect to DCPD units). The reaction took place in dark, for 24 h; the modified polymer was subsequently precipitated in ET, washed so that to remove all non-reacted bromide, filtered and dried.

Polymerization of NVKZ using ATRP: A mixture consisting in 0.0198g CuCl, 0.039 g brominated polymer and 0.8 ml ANI has been put into a polymerization vial; after an inert atmosphere was assured by purging with dry nitrogen for 15 minutes; this operation was followed by injecting the complexing agent, namely a solution of

0.096g Byp in 0.2 ml ANI. Subsequently, the vial was sealed off and kept at 80°C for 15 hours. The resulting grafted polymer was separated by precipitation in ET, filtered and dried.

2.3 Product characterization

The initial support polymers, as well as their derivatives have been characterized by FT-IR (Shimadzu 8900 apparatus, in the range 4000-400 cm^{-1} , with a resolution of 2 cm^{-1}). UV spectra were recorded in THF, with a Cintra 101 equipment. The elemental composition has been established by using a multi-EA 3100 apparatus.

Molecular weights were appreciated by GPC (Waters 510-type apparatus, THF as solvent).

DSC measurements have been carried out on a power-compensated DSC calorimeter (Pyris Diamond); scanning was performed under a nitrogen cushion, with a rate of 20 K/min. Prior to the measurements, the calorimeter has been calibrated with Indium.

Thermal decomposition temperature has been found by using a Mettler Toledo TGA-SDTA851 apparatus; the heating rate was 10K/min.

3. Results and discussion

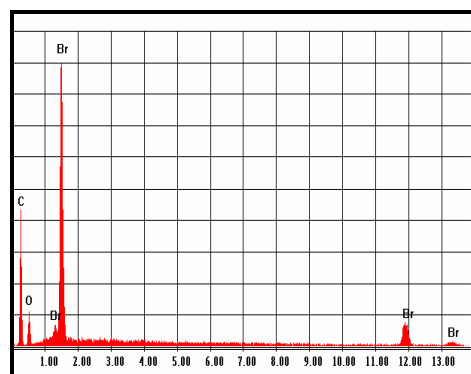
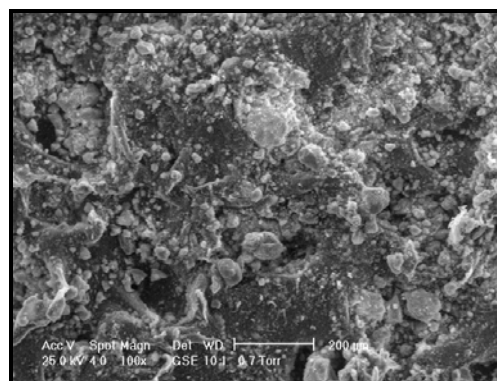
Grafting conversions onto polymer supports depend mainly on the number of the active positions (brominating degree); in other words, the fraction of double bonds (resulted from DCPD) within the main chain, becomes paramount for the grafting extent.

For the binary copolymer, its alternating structure has been previously reported by us [3-6]. We have submitted the ternary copolymer to elemental analysis and found 50% repeat units from MA, 15% from DCPD and 35% IN units, respectively; these percentages are molar ones.

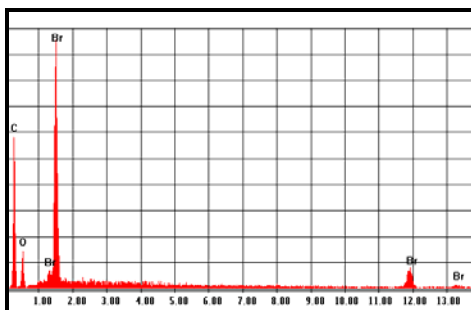
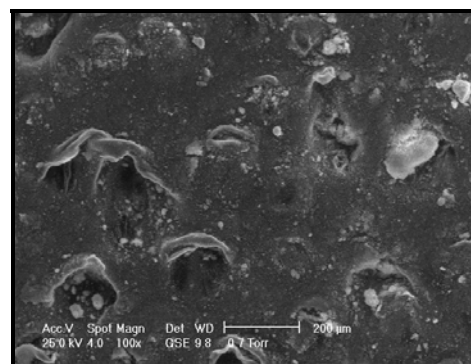
Brominating of support polymers has been put into evidence by SEM, equipped with EDX probe, useful to establish the composition at the material surface (see Figure 1).

Our calculations have shown that for the binary copolymer the brominating degree is around 50% (with respect to DCPD units). For the ternary copolymer, this value decreases to 34%; this fact is to be explained by the lower content of DCPD, the only unit able to add the halogen.

Both polymer supports have been submitted to the reaction involving halogen transfer, so that to graft PNVKZ chains. A qualitative attempt to check the grafting of PNVKZ consisted in recording FTIR spectra. Fig. 2 presents a comparison between the spectra of binary MA-DCPD copolymer and that of the grafted copolymer, respectively.



(a)



(b)

Fig.1. SEM and EDX for brominated derivatives: a) Brominated MA-DCPD copolymer; b) Brominated MA-DCPD-IN ternary copolymer.

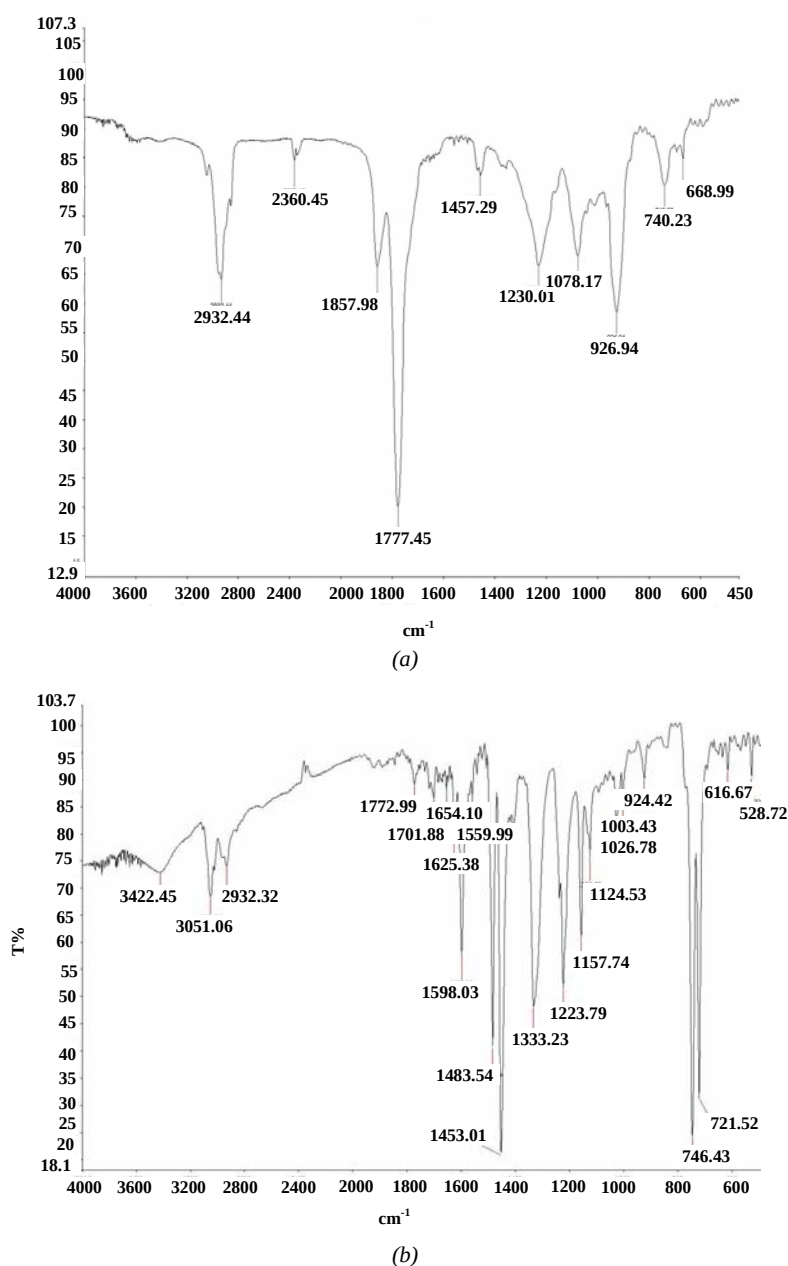


Fig. 2. FT-IR spectra: (a) FT-IR spectrum for MA-DCPD copolymer; (b) FT-IR spectrum for MA-DCPD grafted with PNVK.

Examining the above mentioned spectra, we have found new peaks such as $\nu_{\text{CH}}=3010\text{--}3040\text{ cm}^{-1}$ (aromatic ring) or $\nu_{\text{C}=\text{C}}=1500\text{ cm}^{-1}$. These facts represent a qualitative evidence for the grafting of poly-NVKZ on the chains of the initial support polymers. However, quantitative data regarding the yield of the grafting can be obtained from UV measurements. Indeed, poly-NVKZ shows a strong absorption at 294 nm that can be used for measuring the amount of poly-NVKZ chains on the grafted copolymer.

Table 1. Specific extinction coefficients ($\text{l/mole}\cdot\text{cm}$) for carbazole derivatives; KZ = carbazole; NVKZ = N-vinyl-carbazole.

Wavelength (nm)	334	331	293	294	256.5	234
KZe	-	-	42000	-	48900	10700
NVKZ	-	-	39500	-	42800	95000
Poly-NVKZ	weak	weak	-	14000	-	-

A typical UV spectrum for a grafted copolymer is illustrated in Fig. 3.

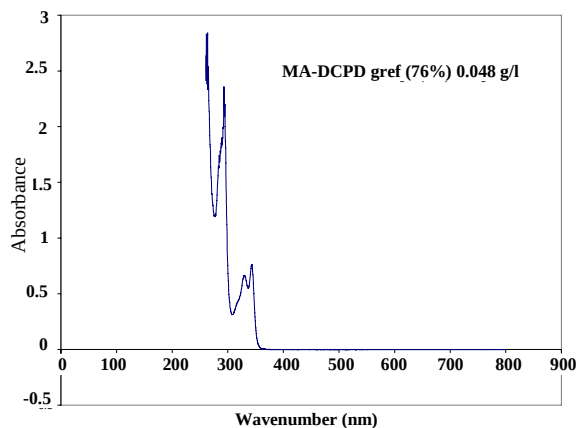


Fig. 3. UV Spectrum for the binary MA-DCPD copolymer after grafting with Poly-NVKZ.

In our study we have measured specific extinction coefficients for carbazole derivatives and found that the monomer (NVKZ) exhibits an even stronger extinction coefficient, in the neighborhood of 294 nm. For this reason, a special attention has been given to the removal of unreacted monomer from the sample (by repeated extractions in ET).

The grafted and monomer-free samples were submitted to UV measurements; the grafting was characterized by yields in the range of 72-81% (w/w), thus proving the accomplishment of grafting.

These results show the adding of 3-4 NVKZ units for each DCPD unit.

A first attempt to assess the thermal resistance consisted in measuring the second order transitions (namely T_g). The corresponding DSC diagrams are presented in Fig. 4.

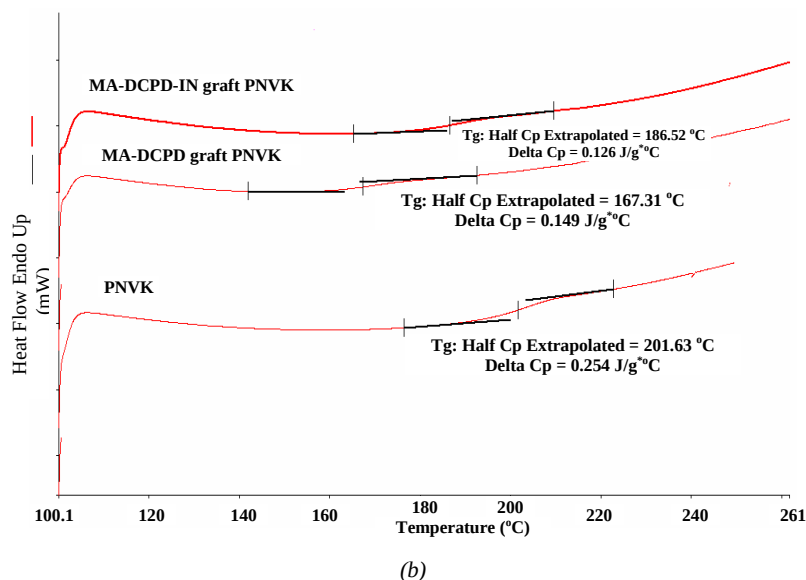
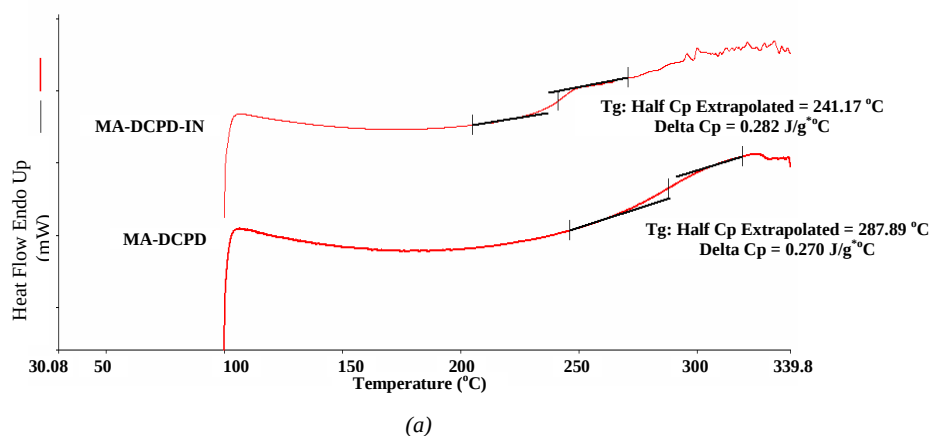


Fig. 4. DSC diagrams.

The grafted copolymers show lower second order transition temperatures than both poly-NVKZ and the initial copolymers; these apparently paradoxes might be explained by the structure of newly formed grafted products. In fact, the initial chains are now more distanced than before grafting; anyway, the length of the new chains is too low, so that to be the source of an increase in T_g values. Consequently, the prevalent effect is that of reducing the initial chain stiffness by diminishing the original chain interactions.

A complete assessment of resistance at high temperatures has implied the assistance of TGA measurements, to put into evidence the capacity for preserving chemical integrity. The results are presented in Fig. 5.

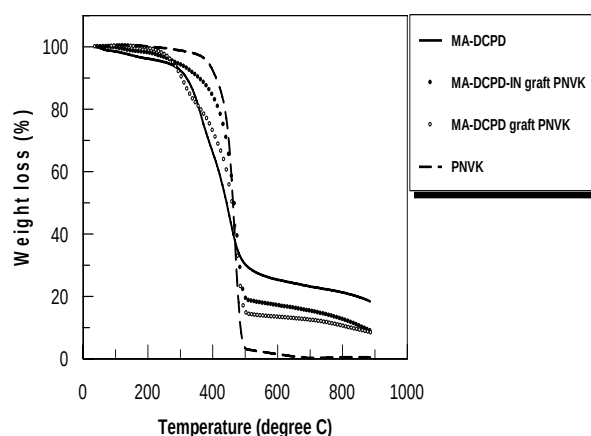


Fig. 5. TGA Analyze on grafted products.

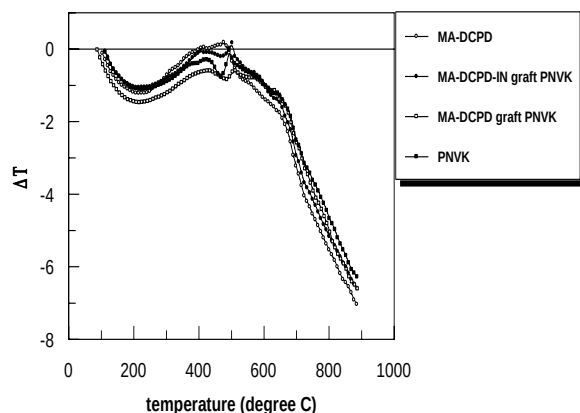


Fig. 6. SDTA Diagram for support polymers and grafted products respectively.

With regard to decomposition kinetics, one can notice that the copolymers containing grafted NVKZ exhibit higher thermal resistances than the initial support polymers. The characteristic temperatures for grafted and non-grafted copolymers are presented in Table 2.

Table 2. Characteristic temperatures for grafted and non-grafted copolymers.

Polymer	T_g ($^{\circ}\text{C}$)	T_{dec} ($^{\circ}\text{C}$)	Weight losses at different temperatures(%)
MA-DCPD	288	445	45.53 (440 $^{\circ}\text{C}$)
MA-DCPD g-PNVKZ	167.31	475	73.71 (475 $^{\circ}\text{C}$)
MA-DCPD-IN	241	-	-
PNVKZ	201.63	467	100 (467 $^{\circ}\text{C}$)

Supplementary evidence with regard to the behavior at temperature rises (200-600 $^{\circ}\text{C}$) has precisely resulted by using SDTA (see figure6).

Thus, for the binary copolymer, a weak exothermal effect has been noticed in the range 400-500 $^{\circ}\text{C}$. This fact may be attributed to the consumption of residual double bonds in the initial copolymer (crosslinking); this phenomenon is drastically reduced for the grafted copolymer and, obviously, is missing in the diagram corresponding to poly-NVKZ.

4. Conclusions

These preliminary results clearly show a significant increase of thermal resistance after grafting NVKZ on polymer supports such as MA-DCPD or MA-DCPD-IN.

TGA diagrams best illustrate the fact that partial replacement of DCPD with IN, followed by NVKZ grafting, substantially improves the conservation of chemical integrity up to 400 $^{\circ}\text{C}$. Further changes in the grafting density and lengths of grafts are expected to introduce supplementary positive effects.

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