Chemical Transformations on Copolymers Obtained from Dicyclopentadiene

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Copolymers based on dicyclopentadiene and maleic anhydride have been reacted with several aromatic amines (typical polymer-analogous reaction) to obtain the corresponding amides, and subsequently imides. An appropriate procedure has been established and the conversion has been appreciated. All the products have been characterized from the structural point of view, as well as by measuring the improved thermal properties.

Keywords: dicyclopentadiene; maleic anhydride; polymer-analogous reaction; thermal properties.

Early scientific works, in the field have shown that dicyclopentadiene (DCPD) may copolymerize with maleic anhydride (MA) through a radical mechanism, even if DCPD cannot homopolymerize [1,2]. The resulting copolymers exhibit a quasi-equimolecular composition, as it has been proved by us [3]; a detailed kinetic investigation has illustrated some peculiarities of the copolymerization process, both in heterogeneous [4] and homogeneous systems [5]. Attempts to produce ternary copolymers (however containing around 50% succinic repeat units) have also been reported [6].

Such works have shown the possibility of using DCPD in polymer production, but unfortunately the resulting copolymers display low molecular weights; in turn, this attribute leads to poor mechanical and thermal properties. However, the above described copolymers may be used for removal of metallic ions from aqueous solutions [7].

Chemical transformation of the alternating copolymer styrene/maleic anhydride (SMA) by reacting with aromatic amines has been described in detail [8-10]. The present paper describes an attempt to improve the thermal properties of DCPD copolymers by using polymer-analogous reactions.

Experimental part

Raw and auxiliary materials

Maleic Anhydride (Merck) was purified by recrystallization from chloroform, indene (Fluka), was purified by distillation, (p= 5mmHg, T=44.3^{0}C), while dicyclopentadiene (Aldrich) was used as such. N-vinyl carbazole (NVK) from Fluka was, purified by recrystallization from methanol.

Aniline (AN) from Merck has been purified by distillation (p=10 mm Hg, t=69.4^{0}C), while cyclo-hexyl-amine (Aldrich) was distilled in a similar manner (p=100 mm Hg, T=69.3^{o}C); 2- amino 4-chloro-6- methyl pyrimidine (PYR), and 4-trifloro-methyl aniline (FA) (Aldrich) have been used as such.

Solvents and non-solvents, namely Dimethylformamide (DMF), Anisole (ANI), Tetra-hydro-furan (THF), Ethyl ether (ET) have been purified by distillation. The initiator chosen (Merck) - Lauroyl peroxide (LP) was purified by recrystallization from ethanol (Aldrich).

Catalyst, namely, triethyl amine (TEA) (Merck) was submitted to distillation, (T=89.7^{0}C); while acetic anhydride (AA), as well as anhydrous sodium acetate (SA) (Chimopar) have been used without further purifications.

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), PL = 5 . 10^{-2}mole/L) in DMF. The reaction has been carried out at 80^{0}C under a nitrogen cushion; after 3 h, 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^{0}C initiated by LP (5 . 10^{-2}mol/L) we found a quasi-total conversion after 3 h; the ternary copolymer was separated after precipitation in ET, followed by filtration, drying and weighting. Consequently, this procedure was similar to those previously reported [6].

Polymer-analogous reactions

The support polymer was dissolved in DMF (10%) together with the corresponding amine (the amount of amine was that equivalent to the number of MA moles contained in the support polymer). Amidation of support polymers has been carried out in a reactor equipped with a stirring device for 3 h, at room temperature; the separation took place by precipitation in ET.

The semi-amides obtained this way were dissolved in DMF (10% w/w) and put in contact with the mixture AA : SA : TEA = 2 : 0.2 : 1 with respect to the number of MA moles, contained within the support polymer. The reaction took place at 60^{0}C for 6 h; then the product was separated by precipitation in ET, filtered and dried.

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}). The elemental composition has been established by using a multi- 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

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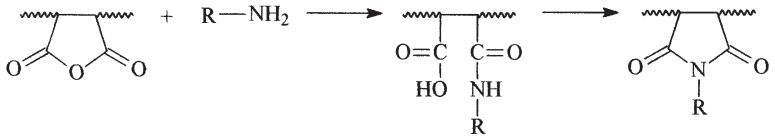


Fig. 1. Consecutive reactions carried out on polymer supports

was performed under a nitrogen cushion, with a rate of 20 degrees/min. Before 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.

Results and discussions

In polymer-analogous reactions, the extent of the reaction depends mainly on the initial composition of the MA-DCPD copolymer, namely on the fraction of succinic anhydride repeat units. For the binary copolymer, its alternating structure has been demonstrated in our previous works [3-5]. For the tertiary copolymer (MA-DCPD-IN), its composition has been established through elemental analysis; we have found 50% repeat units from MA, 15% DCPD and 35% IN, respectively.

All polymer-analogous reactions described in the present paper involve anhydride functions; the succession of reactions is illustrated in figure 1.

The first step consisted in a qualitative estimation of changes that have occurred on polymer supports. In this respect, a valuable tool is FT-IR spectroscopy, that allowed us to put into evidence the distinctive peaks for amide and imide functions, respectively. The results are summarized in table 1.

Inspecting the synthetic data presented in table 1, it is easy to notice the decrease of peaks corresponding to the anhydride ring ($\nu_{C=O}$ 1778, 1858 cm^{-1}) **(I)** and the existence of new peaks (δ_{OH} and δ_{NH} at 3200 – 3600 cm^{-1} **(IV)**, $\nu_{C=O}$ from the acid 1720 cm^{-1}, $\nu_{C=O}$ amide I 1660 cm^{-1}, ν_{CN} amide II 1540 cm^{-1}**(V)**, thus confirming the amidation that has taken place.

Likewise, the newly synthesized imide structures are characterized by the loss of the peak situated at 1540 cm^{-1} corresponding to ν_{CN} amide II and the augmenting peaks $\nu_{C=O}$ imide 1780 cm^{-1} and 720 cm^{-1}, ν_{CN} 1370 cm^{-1}**(VII)**. However, for both polymer supports (the binary copolymer MA-DCPD and the ternary copolymer MA-DCPD-IN, respectively) the peaks typical for DCPD ($\nu_{C=C}$ 1614 cm^{-1} and 1640 cm^{-1} characteristic for the double bond in the five-member-ring and seven-member ring in that order **(II)**) are maintained; furthermore, the peaks representative for IN (3063 cm^{-1} vibration ν_{C-H}, 1600 cm^{-1} $\nu_{C=C}$, from aromatic ring **(III)**) are also kept.

Table 1 reveals also the characteristic peaks for co-reactants **(VI, VIII, IX)**.

Table 1

FT-IR DATA (CHARACTERISTIC PEAKS FOR THE PRODUCTS OBTAINED)

Polymer	Distinctive peaks			
MA-DCPD	$\nu_{C=O}$ 1778, 1858 cm^{-1}(I)		$\nu_{C=C}$ 1614 cm^{-1}, 1640 cm^{-1}(II)	
MA-DCPD-IN	(I), (II)		ν_{C-H} 3063 cm^{-1}, $\nu_{C=C}$ 1600 cm^{-1}(III)	
MA-DCPD (amide with AN)	δ_{OH}, δ_{NH} 3200 – 3600 cm^{-1}(IV)	(I), (II)	$\nu_{C=O}$ 1720 cm^{-1}, $\nu_{C=O}$ amide I 1660 cm^{-1}, ν_{CN} amide II 1540 cm^{-1}(V)	$\nu_{C=C}$ 1500 cm^{-1} γ_{CH} 756 cm^{-1} aromatic ring (VI)
MA-DCPD (imide with AN)	(I), (II)		$\nu_{C=O}$ imide 1780 cm^{-1} si 720 cm^{-1}, ν_{CN} 1370 cm^{-1}(VII)	(VI)
MA-DCPD (amide with CHA)	(I), (II), (IV), (V)			δ_{CH2} 1452 cm^{-1} in ciclohexane (VIII)
MA-DCPD (imide with CHA)	(I), (II),(VII)		(VIII)	
MA-DCPD (amide with PYR)	(I), (II), (IV), (V)			$\nu_{C=H}$ 3020 cm^{-1}, $\nu_{C=C}$ 1637 cm^{-1}, ν_{C-N} 1570 cm^{-1} (IX)
MA-DCPD (imide with PYR)	(I), (II),(VII)		(IX)	
MA-DCPD (amide with FA)	(I), (II),(IV), (V)			(VI)
MA-DCPD (imide with FA)	(I), (II), (VII)			(VI)
MA-DCPD-IN (amide with AN)	(I), (II), (III),(IV),(V)			(VI)
MA-DCPD-IN (imide with AN)	(I), (II),(III), (VII)			(VI)
MA-DCPD-IN (amide with CHA)	(I), (II), (III), (IV), (V)			(VIII)
MA-DCPD-IN (imide with CHA)	(I), (II), (III), (VII)			(VIII)
MA-DCPD-IN (amide with PYR)	(I), (II), (III),(IV), (V)			(IX)
MA-DCPD-IN (imide with PYR)	(I), (II), (III),(VII)			(IX)
MA-DCPD-IN (amide with FA)	(I), (II), (III), (IV), (V)			(VI)
MA-DCPD-IN (imide with FA)	(I), (II), (III),(VII)			(VI)

Table 2
DATA OBTAINED BY ELEMENTAL ANALYSIS

Polymer	C %	H %	N %	Extent of reaction*
MA-DCPD (CHA amide)	73.10	6.98	2.08	40%
MA-DCPD (PYR amide)	66.28	3.92	5.53	36%
MA-DCPD (AN amide)	73.55	4.60	1.30	33%
MA-DCPD (FA amide)	69.42	5.67	1.50	30%
MA-DCPD-IN (CHA amide)	74.06	7.59	2.50	46%
MA-DCPD-IN (PYR amide)	65.35	5.89	6.29	42%
MA-DCPD-IN (AN amide)	73.62	6.27	2.00	38%
MA-DCPD-IN (FA amide)	68.93	5.62	1.71	35%
MA-DCPD (CHA imide)	73.13	6.65	2.24	20%
MA-DCPD (PYR imide)	66.94	3.73	6.01	18%
MA-DCPD (AN imide)	74.29	4.38	1.41	16%
MA-DCPD (FA imide)	70.12	5.40	1.63	15%
MA-DCPD-IN (CHA imide)	74.88	7.23	2.71	22%
MA-DCPD-IN (PYR imide)	66.01	5.61	2.80	20%
MA-DCPD-IN (AN imide)	74.29	4.38	2.17	19%
MA-DCPD-IN (FA imide)	69.62	5.35	1.85	18%

*with respect to 100 moles of MA

As a result of polymer-analogous reactions (until a given conversion) the solubility of polymer products slightly changes, so that appreciating the extent of reaction only by gravimetric means represents a uncertain way out. Instead, we have preferred to submit the samples to elemental analysis; indeed, in the first stage, the increase in nitrogen content corresponds to the degree of amidation of anhydride groups. The results are shown in table 2.

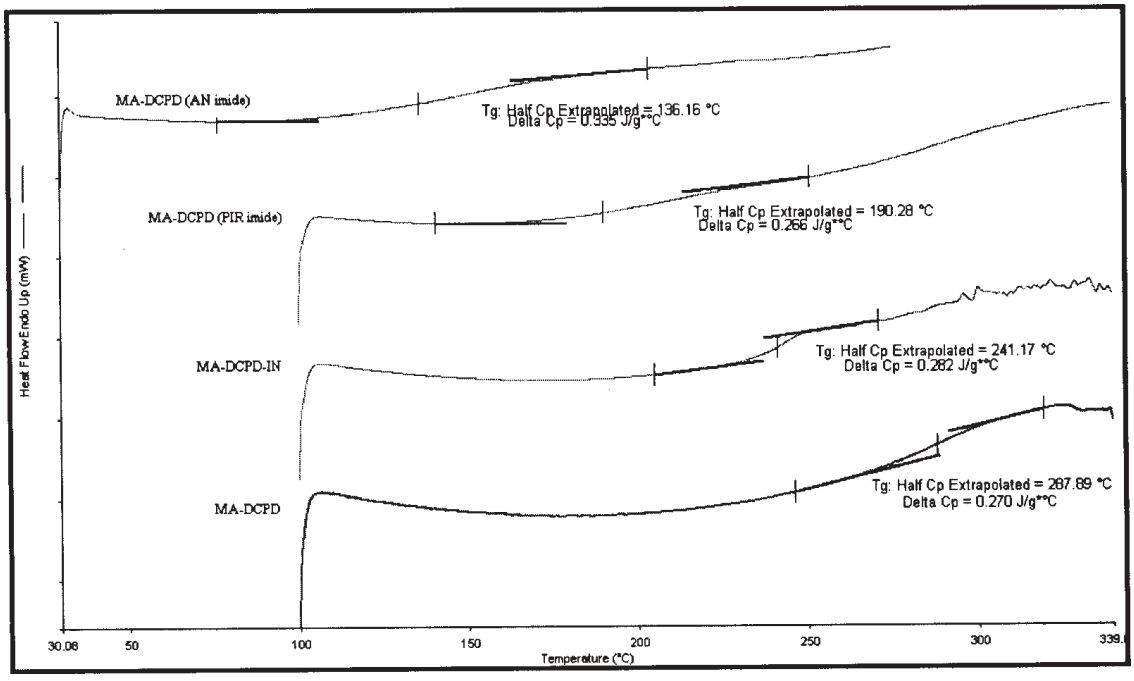
Examining the data from table 2, a semi-amidation degree in the range 30 - 46% is observable for the polymers studied; this fact may be explained by reaching a ceiling conversion [8, 10]. A comparison may be made either between the two polymer-supports, or among the derivatives obtained from the same polymer-support.

Consequently, we have found a growth of the semi-amidation degree with the increasing basicity of the amine used both for the binary and ternary copolymers, respectively. Comparing the two copolymers we have noticed better results for the ternary one: this remark might be explained by the conformational difference and less by the discrepancy in molecular weights for the two copolymers. The molecular masses ($M_{n\ MA\text{-}DCPD}$ = 2 800, $M_{n\ MA\text{-}DCPD\text{-}IN}$ = 6 500) sustain the above assertions.

The different accessibility of the small molecule (amine) to the reactive groups on the polymer chain might be explained by the more accentuated rigidity, inherent to the ternary copolymer; undeniably, in this situation the reactive groups from the chain are more exposed for the co-reactant then for a coiled conformation (case of the binary copolymer). We do not eliminate the presumption regarding the effect introduced by the mixture solvent/co-reactant on solvated copolymer conformation.

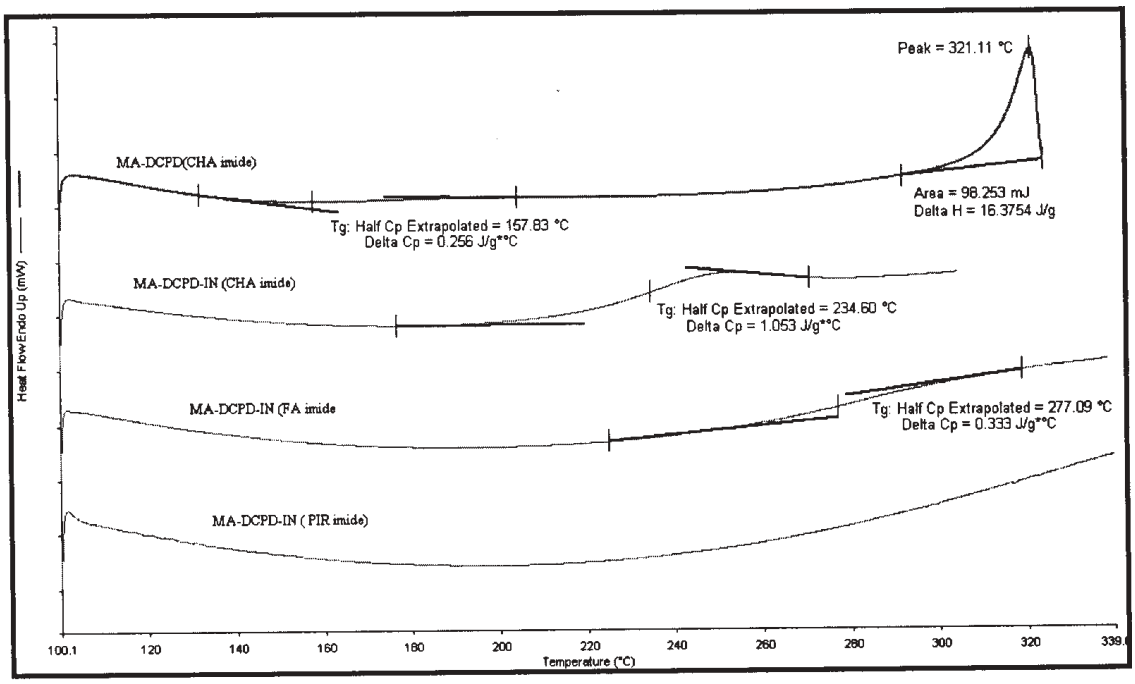
A first attempt to appreciate the thermo-resistance consisted in measuring second-order transitions (DSC assessments), as Tg is the boundary from rigid-amorphous body to flexible-amorphous body. DSC diagrams are shown in figure 2.

In the present work, an important concern was that to improve the thermal properties of copolymers obtained from DCPD. It seems that for the analogous derivatives of the terpolymer, the chemical transformations may increase



a)

Fig. 2a. DSC Diagrams



b)

Fig. 2b. DSC Diagrams

the chain rigidity, and consequently the augmentation of the upper temperature in current use.

Obviously, a complete assessment of thermal resistance at high temperature has implied TGA measurements; this way we have put into evidence the capacity to preserve their chemical integrity with the temperature raise, for the polymers synthesized. The results are presented in figure 3.

We have noticed important distinctions with respect to the kinetics of thermal decomposition, both for the initial copolymers, as well as for imide derivatives. Anyway, it is obvious that imide derivatives obtained from the ternary copolymer exhibit a far better thermal resistance in comparison with all the other polymers.

A supplementary confirmation regarding the behaviour for high temperature rises (200-600^{0}C) has been obtained by using SDTA. Thus, for specimens submitted to analysis we have noticed a weak exothermal process (in the range 200-400^{0}C), that may be attributed to the consumption of the residual double bonds within the polymer

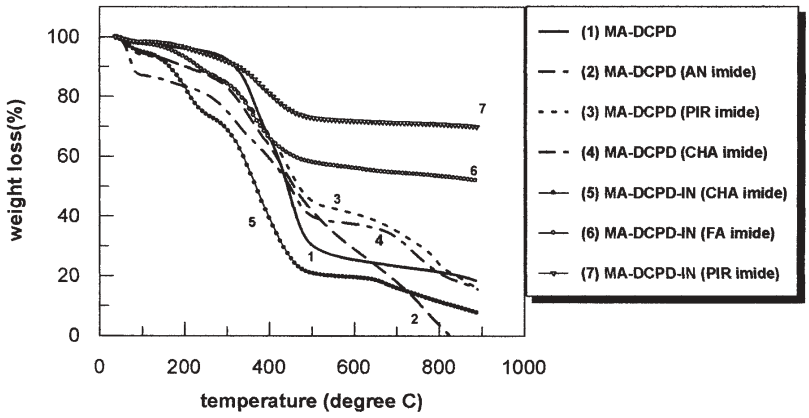


Fig. 3. TGA analysis

Table 3

CHARACTERISTIC TEMPERATURES FOR POLYMER-ANALOGOUS DERIVATIVES

Polymer	Tg (^{o}C)	Tg (^{o}C)$^{-}$	Weight losses at different temperatures (%)		
MA-DCPD	288	445	-	-	43.53 (450^{0}C)
MA-DCPD (AN imide)	137	858	9.84(170^{0}C)	58.50(353^{0}C)	32(767^{0}C)
MA-DCPD (PIR imide)	190	804	7.78(171^{0}C)	47.53(442^{0}C)	23.36(791^{0}C)
MA-DCPD (CHA imide)	158	808	4.5(163^{0}C)	18.74(324^{0}C)	22.13(731^{0}C)
MA-DCPD-IN (CHA imide)	235	692	22(205^{0}C)	53.71(375^{0}C)	12.12(676^{0}C)
MA-DCPD-IN (FA imide)	277	456	12.14(227^{0}C)	33.71(357^{0}C)	-
MA-DCPD-IN (PIR imide)	-	479	8.82(284^{0}C)	19.85(371^{0}C)	-
MA-DCPD-IN	241	-	-	-	-

(crosslinking). However, the partial overlapping of this process with the beginning of endothermic decomposition makes difficult the task of an accurate understanding of these results. Anyway, both for SDTA as well as for TGA are significant so that to put into evidence the weigh losses accompanied by endothermic effects. The main results are presented in table 3.

Studying the values presented in table 3, for each compound synthesized one may find several steps during thermal degradation. Thus, three temperature ranges, namely: **a**-(170^{0}C-230^{0}C), **b**-(350^0-400^{0}C), **c-(>**450^{0}C) are typical for all polymers. The first range may be attributed to imidization or secondary amidation reactions, while the second is due to homo-lithic or hetero-lithic degradation at substituent level; obviously, the last one represents the destruction of the main chain.

Conclusions

The copolymers based on dicyclopentadiene and maleic anhydride have been transformed into the corresponding amides and imides respectively, by reacting them with several aromatic amines.

All the derivatives obtained have been characterized by elemental analysis, FT-IR, DSC and DTG.

As a result of amidation (imidization), the thermal resistance of the initial copolymers is much improved.

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