

# Esterification of ethylene-vinyl alcohol copolymers in homogeneous phase using *N,N'*-dimethylpropyleneurea as solvent

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## Abstract

Ethylene-vinyl alcohol copolymers (EVAL) were esterified with 3,5-dinitrobenzoyl chloride using the cyclic urea *N,N'*-dimethylpropyleneurea (1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone) (DMPU) as the solvent. Ethylene-vinyl alcohol-vinyl-3,5-dinitrobenzoate terpolymers (EVALVDNB) and ethylene-vinyl-3,5-dinitrobenzoate copolymers (EVDNB) were obtained. Both EVAL copolymers (6–73 mol% VAL) and esterified polymers, EVDNB, and EVALVDNB dissolve in DMPU. The substitution may become total under the experimental conditions. The degree of transformation was determined by <sup>1</sup>H NMR. EVDNB copolymers were characterised by IR spectroscopy and <sup>1</sup>H and <sup>13</sup>C NMR. Thermal properties were studied by DSC. The glass transition temperature of the EVDNB copolymers having a low VDNB content (up to 14 mol%) is roughly constant, whereas above 50 mol% increases. Melting temperature decreases as the VDNB content is increased, owing to the fact that the VDNB groups are excluded from the polyethylene crystal lattice.

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## 1. Introduction

The synthesis of polymers performed by modification of some commercially available polymers has always received much attention for industry and science. Poly(vinyl alcohol) (PVAL) and copolymers of vinyl alcohol, poly(ethylene-*co*-vinyl alcohol) (EVAL), are especially suitable for that purpose because they can be easily modified through its hydroxylic groups.

The esterification of PVAL and EVAL copolymers in order to prepare poly(vinyl esters) and vinyl esters copolymers have been carried out by reacting the polymer with an acyl chloride. It has been found that the method of preparing poly(vinyl alcohol esters) by reacting PVAL or EVAL copolymers with an acyl chloride often results in complications.

In esterification of PVAL or EVAL copolymers it is important to obtain full substitution of hydroxyl groups to prepare the required poly(vinyl esters) or ethylene vinyl

ester copolymers. Esterification reactions under homogeneous conditions demand complete dissolution of PVAL or EVAL and its esters in an appropriate solvent. It is difficult to find an inert solvent for EVAL copolymers. EVAL copolymers with a medium and a high content of VAL can be dissolved in very polar solvents such as *N*-methyl-2-pyrrolidone (NMP) or dimethylsulfoxide (DMSO), but those copolymers with low content of VAL are insoluble in NMP or DMSO.

NMP has been used as solvent for esterification of EVAL copolymers containing high alcohol contents (71 mol%) [1] with acyl chlorides, achieving total esterification. On the other hand, the esterification of an EVAL copolymer (60 mol% vinyl alcohol) carried out in heterogeneous phase using *N,N*-dimethylformamide (DMF) [2] leads to a partial modification of EVAL copolymer.

In the present work, ethylene/vinyl ester copolymers were synthesised through the homogeneous esterification of EVAL copolymers with 3,5-dinitrobenzoyl chloride in a dipolar aprotic solvent, the cyclic urea *N,N'*-dimethylpropyleneurea (1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone, DMPU). DMPU is an excellent polymer solvent and

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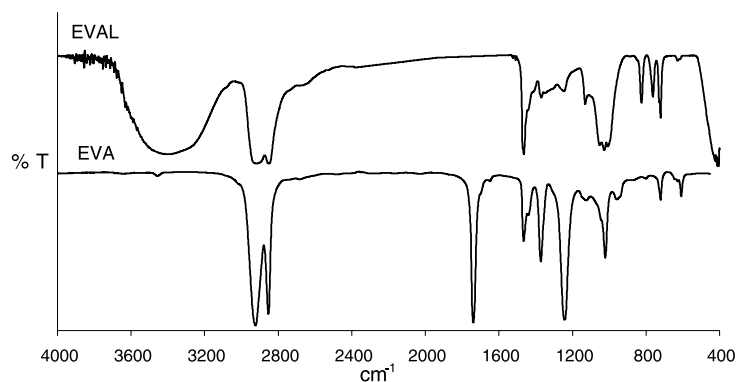


Fig. 1. FTIR spectra of EVA (10 mol% VA) and EVAL (10 mol% VAL).

EVAL copolymers having low and high alcohol content, and their esters display excellent solubility in it. In this paper we will describe some of our results regarding the use of DMPU to exemplify the utility of this solvent for ethylene/vinyl esters synthesis from EVAL copolymers with acyl chlorides.

## 2. Experimental

### 2.1. Materials and methods

Commercially available ethylene-vinyl acetate copolymers (EVA) (vinyl acetate contents 6, 10 and 14 mol%)

(from Repsol YPF), ethylene-vinyl alcohol copolymers (EVAL) (vinyl alcohol content 50 mol% (Polysciences) and 56, 62, 68 and 73 mol% (Aldrich)), poly(vinyl acetate) (PVA) ( $M_w=90,000$ ) and poly(vinyl alcohol) (PVAL) ( $M_w=108,000$ ) (Polysciences), 3,5-dinitrobenzoyl chloride (DNBC) (Fluka), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) (Fluka), 1-methyl-2-pyrrolidone (NMP) (Fluka), pyridine (Fluka), were used without further purification.

The IR spectra were recorded on a Perkin–Elmer 2000 FTIR spectrophotometer using polymer films on NaCl discs. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained with a 300 MHz Brüker Avance DPX-300 spectrometer. DSC measurements were performed on a Polymer Laboratories

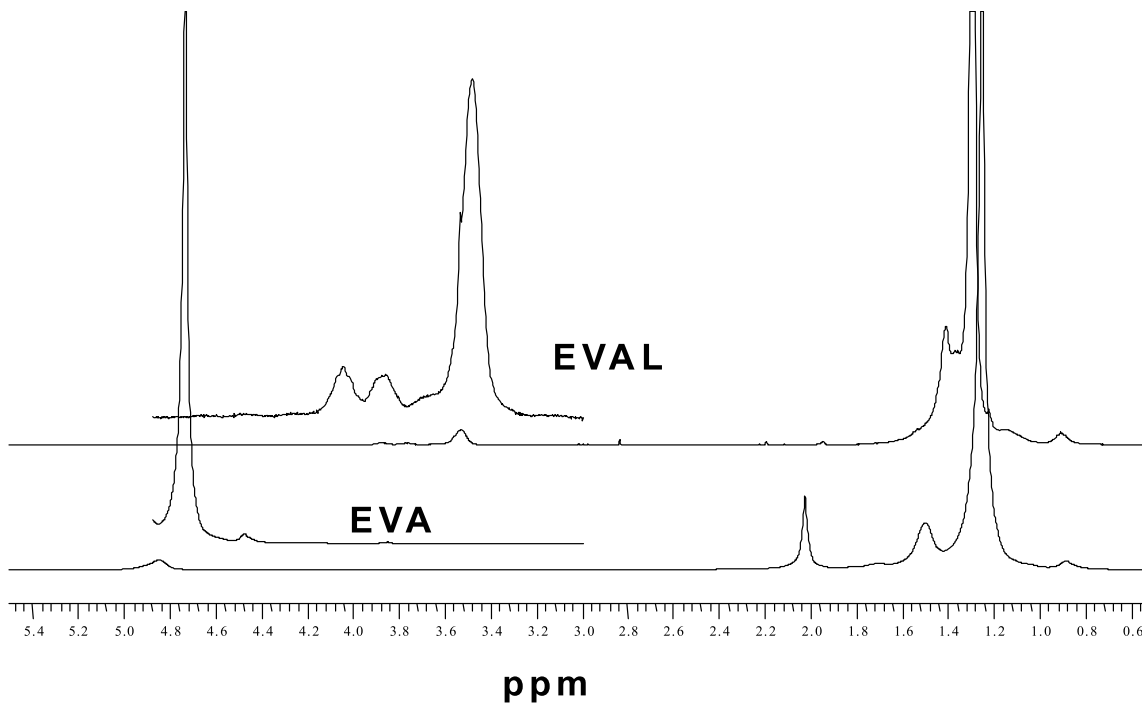


Fig. 2. 300-MHz  $^1\text{H}$  NMR spectrum of EVA (10 mol% VA) showing the amplified region of the methine protons adjacent to the acetate groups, and EVAL (10 mol% VAL) showing the amplified region of the methine and hydroxyl protons.

Table 1  
Chemical shifts of  $^1\text{H}$  and  $^{13}\text{C}$  resonance lines for EVA copolymer

$^1\text{H}$ chemical shift (ppm)	Proton	$^{13}\text{C}$ chemical shift (ppm)	Carbon	Triads
0.87	$\text{CH}_3$ (E)	21.08	$\text{CH}_3$ (V)	VEV
1.25	$\text{CH}_2$ (E)	25.3	$\text{CH}_2$	VEE, EEV
1.49	$\text{CH}_2$ (V)	29.5, 29.64	$\text{CH}_2$	EEV, EEE
2.02	$\text{CH}_3$ (V)	34.15	$\text{CH}_2$	EEV, EVE, VEV, VEE
4.85	$\text{CH}$ (V)	70.35, 71.39	$\text{CH}$	EVV, VVE
		74.02, 74.39	$\text{CH}$	EVE
		170.35	$\text{C}=\text{O}$	VVE, EVV
		170.58	$\text{C}=\text{O}$	EVE

E denotes ethylene unit and V vinyl acetate unit.

DSC, connected to a cooling system and calibrated with different standards. The scanning rate used was  $20\text{ }^\circ\text{C}/\text{min}$  and the glass transition temperature ( $T_g$ ) was taken as the initial onset of the change of the slope in the DSC curve. Melting temperature ( $T_m$ ) values were determined as the peak temperature of the whole melting endotherm from the scans made at a heating rate of  $20\text{ }^\circ\text{C}/\text{min}$  under a nitrogen atmosphere.

## 2.2. EVAL synthesis

Ethylene-vinyl alcohol copolymers were prepared by a homogeneous transesterification process, performed using toluene as inert solvent and methanol–sodium methoxide as a reagent for the ester–alcohol transformation, starting from an EVA copolymer.

The EVA copolymer was dissolved in toluene at  $60\text{ }^\circ\text{C}$ . Then the transesterification agent (sodium-methylated

solution in methanol) was added, and the reaction mixture was stirred for about 3 h. Thereafter the solution was neutralised with acetic acid. The reaction mixture was concentrated by evaporation of methanol and toluene and the polymer precipitate. The precipitate was washed with methanol and water and dried under vacuum.

## 2.3. Characterisation of EVA and EVAL copolymers

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of EVA copolymers were registered in  $\text{CDCl}_3$  with TMS as the internal standard, and those of EVALs in 1,2,4-trichlorobenzene (TCB) with benzene- $\text{d}_6$  as the lock material or  $\text{DMSO-d}_6$  with TMS as the internal standard.

The composition of EVA copolymers was determined by  $^1\text{H}$  NMR using the Eq. (1):

$$(\text{VA}) = 4/(A_{\text{CH}_2}/A_{\text{CH}}) + 2 \quad (1)$$

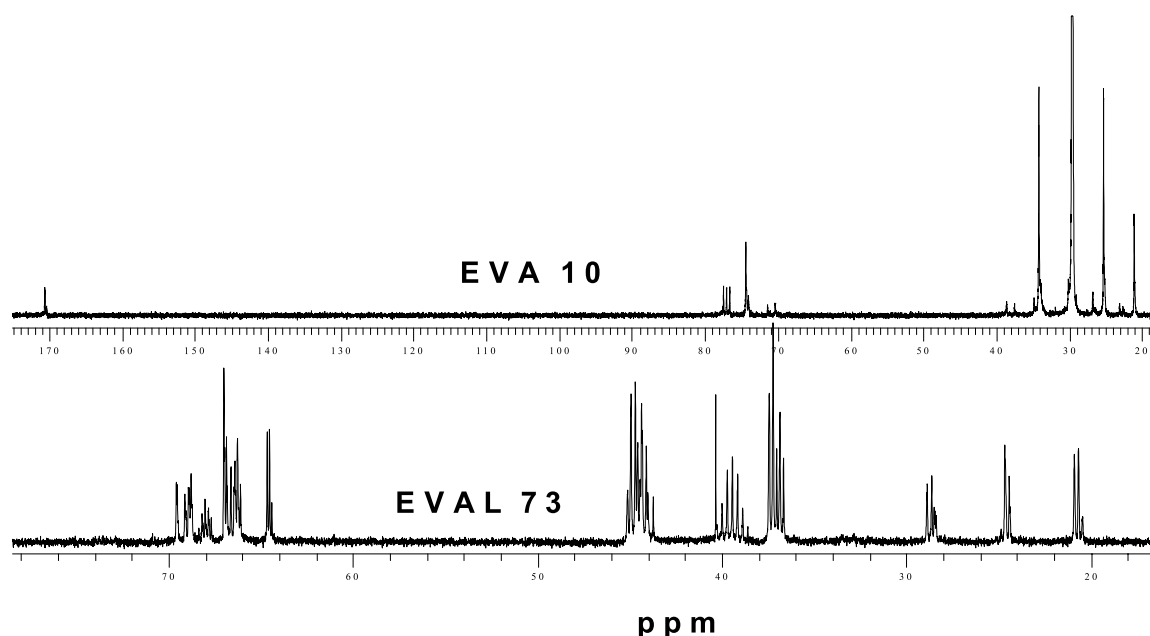


Fig. 3. 300-MHz  $^{13}\text{C}$  NMR spectrum of EVA (10 mol% VA) and EVAL (73 mol% VAL).

Table 2  
Monomer sequence distributions in EVA copolymer (10 mol% VA)

	Triads		
	EVE	VVE+EVV	VVV
Methine	0.88	0.12	0
Carbonyl	0.864	0.14	0

where VA is the mol% of vinyl acetate,  $A_{CH_2}$  represents the total peak area of methylene protons and  $A_{CH}$  the total peak area of methine protons.

The modification extent of the transesterification reaction was determined by  $^1H$  NMR by using the Eq. (2) [3]:

$$(VAL) = 2A_{CH+OH}/(A_{CH+OH} + A_{CH_2}) \quad (2)$$

where VAL is the mol% of vinyl alcohol,  $A_{CH+OH}$  represents the total peak area of methine and hydroxyl protons and  $A_{CH_2}$  the total peak area of methylene protons.

#### 2.4. Reaction of EVAL copolymers with 3,5-dinitrobenzoyl chloride

EVAL copolymers (1 g) were dissolved in DMPU (25 ml) at 80–90 °C, then a definite amount of DNBC was added slowly while stirring at 25 °C. All the reactions were performed at constant temperature, and the polymer remained soluble throughout the process. The modification extent was controlled by the amount of DNBC used. After a definite reaction time the modified polymer was isolated by precipitation using methanol as precipitant, then it was purified by reprecipitation using THF as solvent and water as precipitant, and finally dried *in vacuo*.

Table 3  
Chemical shifts of  $^1H$  and  $^{13}C$  resonance lines for EVAL copolymer (73 mol% VAL)

$^1H$ chemical shift (ppm)	Proton	Triads	$^{13}C$ chemical shift (ppm)	Carbon	Triads
0.84	$CH_3$ (PE branches)		69.6	$CH$ K	EAE
1.24	$CH_2$ (E) (A)		68.7–69.1	$CH$ J	m EAA
1.34					
1.41					
3.37	$CH$	EAE	67.6–68.4	$CH$ I	mmAAA
3.63	$CH$	EAA	66.6–67	$CH$ H	r EAA
3.73–3.74	$OH$	EAE	66.1–66.4	$CH$ G	mr AAA
3.85	$OH$	r EAA	64.4–64.6	$CH$ F	rr AAA
	$CH$	AAA			
3.95	$OH$	rr AAA	43.7–45.1	$CH_2$ E	AA
4.10	$OH$	m EAA	36.6–37.4	$CH_2$ D	EA
4.16–4.17	$OH$	mr AAA	28.4–28.8	$CH_2$ C	EEE
4.34	$OH$	mm AAA	24.4–24.7	$CH_2$ B	AEE
			20.5–20.9	$CH_2$ A	AEA

E denotes ethylene unit and A vinyl alcohol unit. *r* and *m* designate *racemic* and *meso* configurations, respectively.

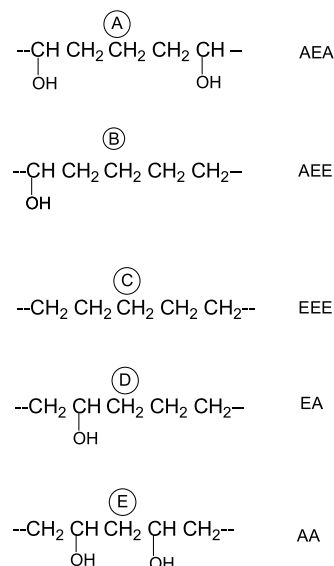


Fig. 4. Structures associated with poly(ethylene-co-vinyl alcohol).

#### 2.5. Characterisation of ethylene-vinyl-3,5-dinitrobenzoate copolymers (EVDNB)

The  $^1H$  NMR and  $^{13}C$  NMR spectra were registered in DMSO- $d_6$  or  $CDCl_3$  with tetramethylsilane (TMS) as internal standard.

The degree of esterification was determined by  $^1H$  NMR using the Eq. (3):

$$(VDNB) = 4/(A_{CH_2}/A_{CH}) + 2 \quad (3)$$

where VDNB is the mol% of vinyl dinitrobenzoate,  $A_{CH_2}$  represents the total peak area of methylene protons and  $A_{CH}$  the total peak area of methine protons.

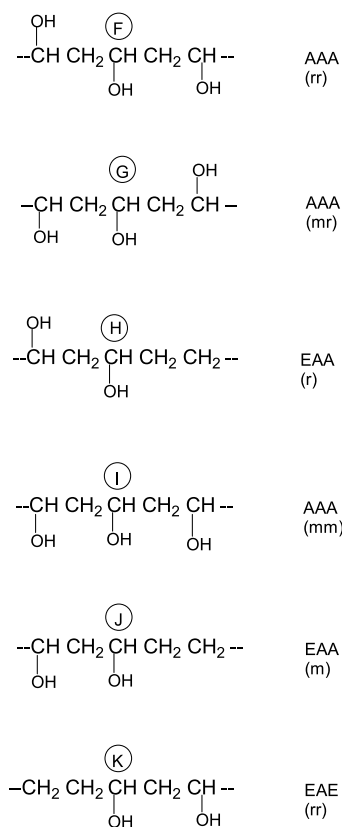


Fig. 5. Structures associated with poly(ethylene-co-vinyl alcohol).

Table 4  
Monomer sequence distributions in EVAL copolymer (73 mol% VAL) from methine proton peaks

Co-monomeric triads		
AAA	AAE	EAE
0.497	0.415	0.087

Table 5  
Monomer sequence distributions in EVAL copolymer (73 mol% VAL) from methine carbon resonances

Co-monomeric triads	mol%
rr AAA	14.4
mr AAA	26.4
r EAA	22.6
mm AAA	9.2
m EAA	20.1
EAE	7.2

Table 6  
Monomer sequence distributions in EVAL copolymer (73 mol% VAL) from methylene carbon resonances

Diads	mol%	Triads	mol%	Block character $\eta$
AA	49	EEE	9.7	0.89
AE	35.2	AEE	38.6	
EE	15.8	AEA	51.7	

### 3. Results and discussion

#### 3.1. Base-catalysed transesterification of EVA copolymers with methanol

EVA copolymers were converted to EVAL copolymers by transesterification with a methanol sodium-methoxide solution, the copolymers obtained were characterised and the total transesterification of EVA copolymers was confirmed by IR spectroscopy, since in all cases the characteristic band at  $3450\text{ cm}^{-1}$  (OH) was observed and the band at  $1735\text{ cm}^{-1}$  was absent as shown in Fig. 1.

In the  $^1\text{H}$  NMR spectra of the transesterified EVA copolymers the signals due to the methyl ( $-\text{CH}_3$ ) (2.02 ppm), and methine protons ( $-\text{CH}$ ) (4.85 ppm) of VA were absent and the signals due to the methine ( $-\text{CH}$ ) and hydroxyl protons of VAL (between 3.4 and 4 ppm) were observed (Fig. 2).

Fig. 3 shows the  $^{13}\text{C}$  NMR spectra of EVA10 and EVAL73. The chemical shifts of  $^1\text{H}$  and  $^{13}\text{C}$  resonance lines for EVA copolymer are given in Table 1 [3,4]. From methine and carbonyl carbon resonances the triads can be calculated [3]. These data are listed in Table 2.

The chemical shifts of  $^1\text{H}$  and  $^{13}\text{C}$  resonance lines for EVAL copolymer are given in Table 3 [5–8], and the corresponding structures are shown in Figs. 4 and 5. From  $^1\text{H}$  NMR spectrum by measuring the methine proton peak intensities the co-monomer triad distributions in EVAL copolymers can be determined [6]. These data are compiled in Table 4. From  $^{13}\text{C}$  NMR spectrum by comparing the methine carbon peak intensities the co-monomer triad distributions in EVAL copolymers can be determined. These data are given in Table 5.

The molar fraction of triads AAA, EAA and EAE are 50, 42.7 and 7.2 mol%, respectively. These values are in agreement with those values obtained from  $^1\text{H}$  NMR spectrum (Table 4).

From  $^{13}\text{C}$  NMR spectrum by comparing the methylene carbon peak intensities the co-monomer diad and triad distributions in EVAL copolymers can be determined [8]. These data are given in Table 6.

Table 6 shows also the block character of the copolymer,  $\eta$ , obtained by the expression:

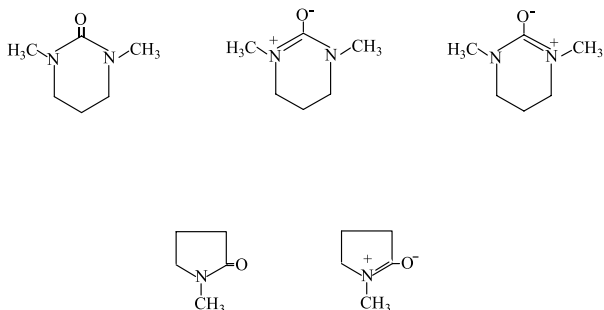
$$\eta = \frac{[\text{AE}]}{2[\text{A}][\text{E}]} \quad (4)$$

where [AE] is the mol fraction of AE diads, [A] and [E] the

Table 7

Esterification of EVAL (73 mol% VAL) with 3,5-dinitrobenzoyl chloride [EVAL]=0.018 mol of hydroxyl group; [DNBC]=0.022 mol

Sample code	Solvent	T (°C)	Time (h)	Degree of esterification (%) <sup>1</sup> H NMR
EVDNB 73.1	DMPU	25	6	90
EVDNB 73.2	DMPU	70	6	99
EVDNB 73.3	DMPU	25	15	90
EVDNB 73.4	DMPU	25	168	95
EVDNB 73.5	NMP <sup>a</sup>	70	7	85

<sup>a</sup> Using pyridine as catalyst, 0.022 mol.

Scheme 1. Major resonance forms of DMPU and NMP.

Table 8

Physical parameters of solvents.  $\mu$  is the dipole moment and  $\epsilon$  is the dielectric constant

Solvent	$\mu$ (D)	$\epsilon$
DMPU <sup>a</sup>	4.23	36.1
NMP <sup>b</sup>	4.09	32.0

<sup>a</sup> Ref. [10].<sup>b</sup> Ref. [11].

mol fractions of vinyl alcohol and ethylene units, respectively.

$\eta$  is a measure of departure from random character [9].  $0 \leq \eta < 1$  is characteristic of block copolymers;  $\eta = 1$  for

random copolymers; the co-monomer tends to alternate in the polymer structure if  $1 < \eta \leq 2$ .

The  $\eta$  value we obtained is close to unity so that the sequence distribution can be regarded as approximately random.

### 3.2. Esterification of EVAL copolymers with 3,5-dinitrobenzoyl chloride

EVAL copolymers were esterified with 3,5-dinitrobenzoyl chloride in a homogeneous medium by solution in DMPU, which serves as both a solvent and an acid binding agent. The experimental results are presented in Table 7. The results show that the total esterification of EVAL copolymer, 73 mol% VAL, took place at 65–70 °C in 6 h. At room temperature the influence of reaction time on degree of modification is negligible and a plateau (90–95%) is reached in 6 h. When comparing the results obtained using DMPU and NMP with pyridine as catalyst (according to the literature method [1]), the maximum extent of modification is obtained with DMPU alone. NMP is not a solvent for EVAL copolymers with low content of VAL (6, 10 and 14 mol%) and the homogeneous esterification of these copolymers must be carried out using DMPU as solvent.

DMPU and NMP are dipolar aprotic solvents with high dipole moments [10,11], attributed to the partial double

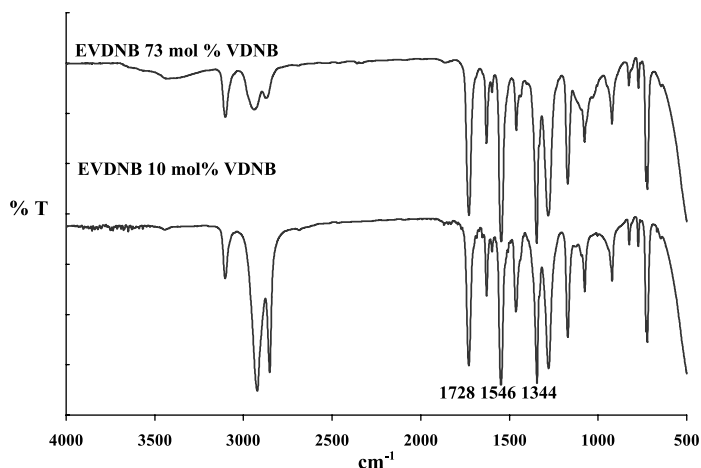


Fig. 6. FTIR spectra of EVDNB (10 mol% VDNB) and EVDNB (73 mol% VDNB).

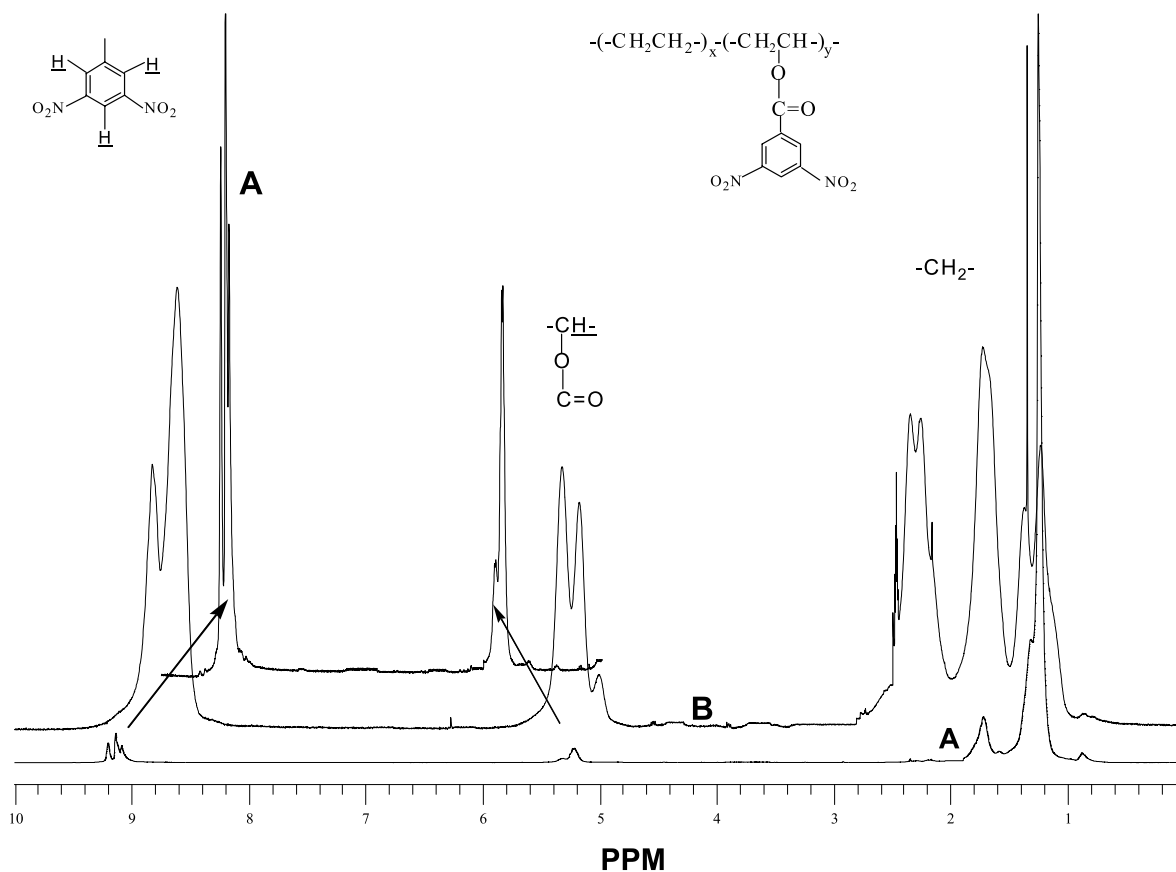


Fig. 7. 300-MHz  $^1\text{H}$  NMR spectra of EVDNB copolymers: (A) 10 mol% VDNB recorded in  $\text{CDCl}_3$ , showing the amplified region of the methine and aromatic protons, (B) 73 mol% VDNB recorded in  $\text{DMSO}-d_6$ .

bond character of its carbonyl carbon–nitrogen bond (Scheme 1). Comparison of the dipole moments and dielectric constants of both shows DMPU has the highest dipole moment and dielectric constant (Table 8). This is the reason for the higher extent of modification obtained with DMPU. Both are strong electron donors or, in other words, good hydrogen acceptors, but DMPU has a higher electron-pair donating ability.

The IR spectra of esterified EVAL copolymers with 3,5-dinitrobenzoylchloride show all the characteristic bands of their chemical modification (Fig. 6). Near  $1730\text{ cm}^{-1}$ , a band assigned to  $\text{C}=\text{O}$  bonds of ester function and at  $1546$  and  $1344\text{ cm}^{-1}$  the bands of  $\text{NO}_2$  assym and  $\text{NO}_2$  sym are observed. The band around  $3450\text{ cm}^{-1}$ , characteristic of hydroxyl functions, disappears which confirm the quantitative substitution of hydroxyl functions.

The  $^1\text{H}$  NMR spectra, Fig. 7, confirms the structures of the polymers. The complete disappearance of the hydroxyl signal between 4 and 4.8 ppm supports a quantitative modification of these functions for reaction at  $65\text{--}70\text{ }^\circ\text{C}$  for 6 h and a dinitrobenzoyl chloride to EVAL molar ratio equal to 1.22. A series of signals can be observed between 4.8 and 5.8 ppm and between 8.2 and 9.3 ppm, attributable to the methine protons and to the aromatic protons in the vinyl dinitrobenzoate group, respectively.

Fig. 8 shows the  $^{13}\text{C}$  NMR spectrum of EVDNB10 and the expansion of the methylene carbon peaks, and the assignments [6] of these lines are indicated on it. These assignments have been done on the basis of the esterification reaction has not effect on tacticity of EVAL copolymers. The corresponding structures are shown in Fig. 9.

Figs. 10 and 11 show the expansion of the methylene and methine region, respectively, of  $^{13}\text{C}$  NMR spectrum of EVDNB73.

### 3.3. Thermal analysis

Prior to the glass transition temperature and the melting point determination, the samples were first heated above the melting point in the DSC, held there for 5 min, then rapidly cooled to  $-150\text{ }^\circ\text{C}$  at the maximum rate possible by the instrument. The glass transition temperatures and the melting points were determined on the subsequent heating thermogram recorded at a heating rate of  $20\text{ }^\circ\text{C}/\text{min}$ .

A typical behaviour of ethylene copolymers in general is that melting pattern consists of multiple components, the main endotherm and shoulders at temperatures well below that may extend below room temperature [12,13]. Fig. 12 shows the DSC melting curves for EVA14 and EVDNB14 samples after annealing at room temperature for several

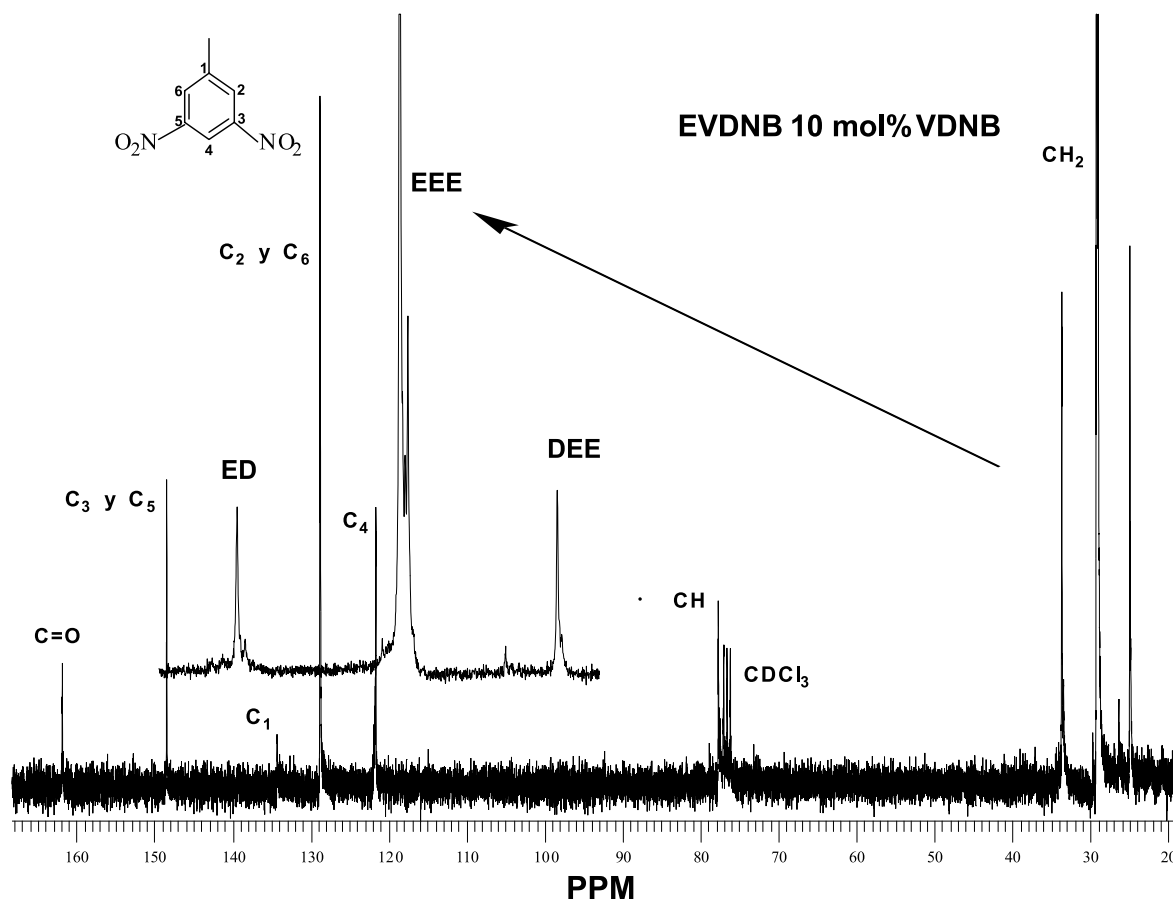


Fig. 8. 300-MHz  $^{13}\text{C}$  NMR spectrum of EVDNB copolymer (10 mol% VDNB) recorded in  $\text{CDCl}_3$ , showing the amplified region of the methylene carbons. E stands for ethylene unit and D for vinyl dinitrobenzoate unit.

days and subsequent quenching to  $-150\text{ }^\circ\text{C}$ . The effects of annealing observed in these copolymers is the appearance of a peak at a temperature around  $40\text{ }^\circ\text{C}$ , i.e.  $20\text{ }^\circ\text{C}$  above the annealing temperature, remaining the main endotherm unaffected. Identical results are found with the other

ethylene copolymer samples studied that show the melting endotherm.

Glass transition and peak melting temperatures are collected in Table 9. The glass transition temperature of the ethylene copolymers studied remains nearly

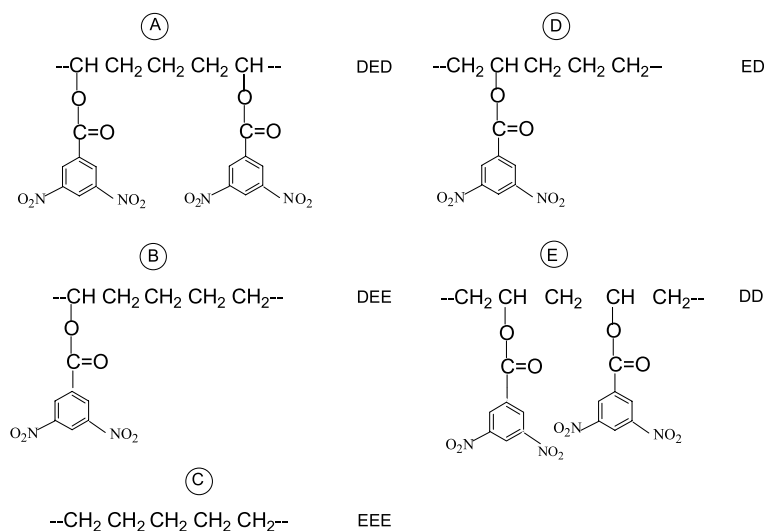


Fig. 9. Structures associated with poly(ethylene-co-vinyl dinitrobenzoate).



## EVDNB 73 mol % VDNB

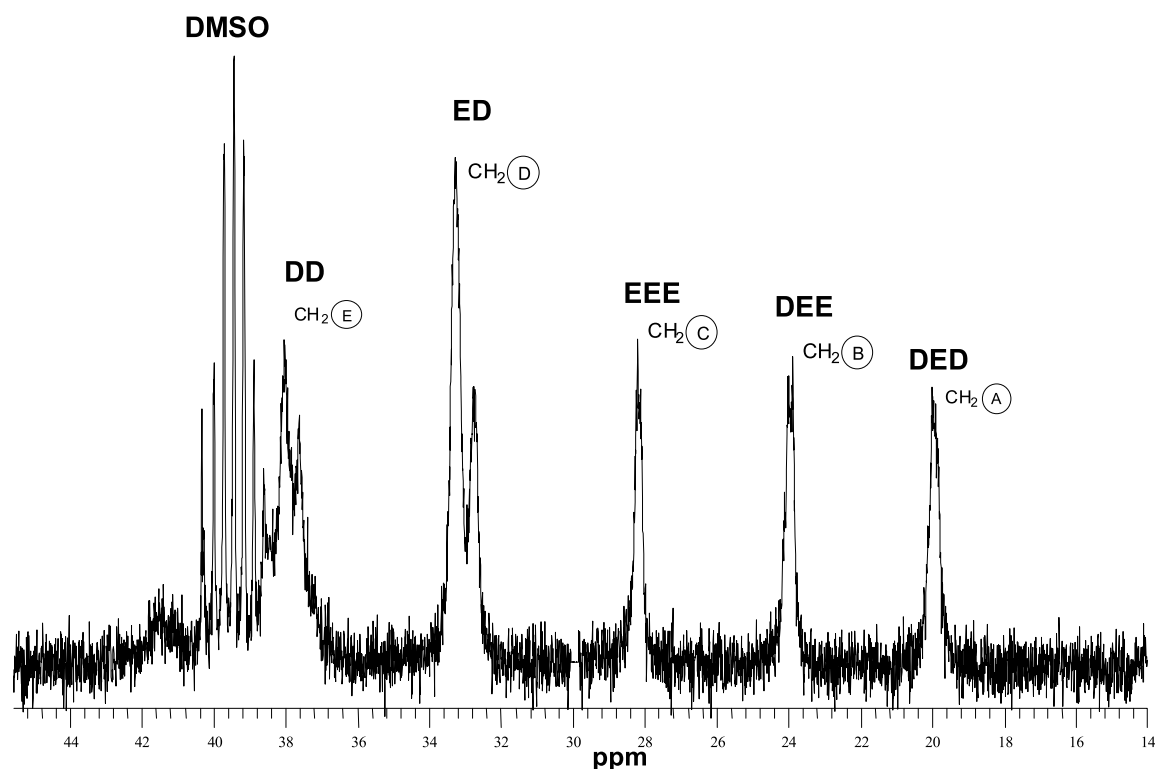


Fig. 10. Amplified region (300-MHz  $^{13}\text{C}$  NMR spectrum) of the methylene carbons for EVDNB copolymer (73 mol% VDNB) recorded in DMSO- $d_6$ . E stands for ethylene unit and D for vinylidinitrobenzoate unit.

Table 9

Glass transition temperatures ( $T_g$ ), and melting temperatures ( $T_m$ ) of PVA, PVAL, EVA, EVAL, and EVDNB copolymers

Sample code	E (mol%)	VA (mol%)	VAL (mol%)	VDNB (mol%)	$T_g$ (°C)	$T_m$ (°C)
EVA2 <sup>a</sup>	98	2	–	–	–41	106
EVA6 <sup>a</sup>	94	6	–	–	–37	90
EVA10 <sup>a</sup>	90	10	–	–	–37	70
EVA14 <sup>a</sup>	86	14	–	–	–41	57
PVA <sup>b</sup>	–	100	–	–	37	–
EVAL6	94	–	6	–	3	103
EVAL10	90	–	10	–	4	107
EVAL14	86	–	14	–	4	108
EVAL50 <sup>b</sup>	50	–	50	–	41	156
EVAL56 <sup>c</sup>	44	–	56	–	46	165
EVAL62 <sup>c</sup>	38	–	62	–	50	169
EVAL68 <sup>c</sup>	32	–	68	–	54	179
EVAL73 <sup>c</sup>	27	–	73	–	55	188
PVAL <sup>b</sup>	–	–	100	–	67	236
EVDNB6	94	–	–	6	2	93
EVDNB10	90	–	–	10	3	67
EVDNB14	86	–	–	14	7	65
EVDNB50	50	–	–	50	79	–
EVDNB56	44	–	–	56	86	–
EVDNB62	38	–	–	62	90	–
EVDNB68	32	–	–	68	100	–
EVDNB73	27	–	–	73	117	–

<sup>a</sup> From Repsol YPF.

<sup>b</sup> From Polysciences.

<sup>c</sup> From Aldrich.

## EVDNB 73 mol % VDNB

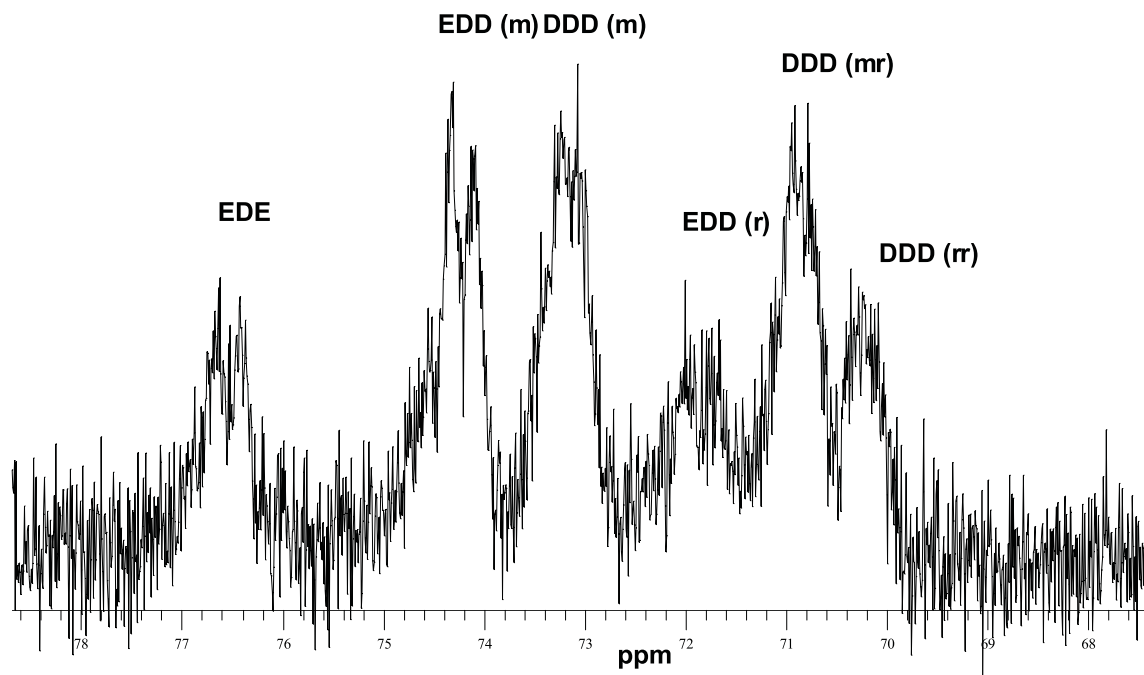


Fig. 11. Amplified region (300-MHz  $^{13}\text{C}$  NMR spectrum) of the methine carbons for EVDNB copolymer (73 mol% VDNB) recorded in  $\text{DMSO-d}_6$ . E stands for ethylene unit and D for vinyl dinitrobenzoate unit.

independent of the copolymer composition, at least in the range of 2–14 mol% of the co-monomer. Thus,  $T_g$  value of EVA copolymers occurs at about  $-39$  and  $4^\circ\text{C}$  for EVAL and EVDNB copolymers. At higher co-monomer contents, above 50 mol%, the glass transition temperature increases, approaching the value for pure homopolymer. The increase of  $45^\circ\text{C}$  in  $T_g$  value brought about by the substitution of

acetate groups for dinitrobenzoate units, is the consequence of a reduction of the mobility of the amorphous phase caused by the bulky dinitrobenzoate side chain groups. The introduction of the hydroxyl groups leads to an increase in  $T_g$  value due to the strong intra- and intermolecular hydrogen bonds which give rise to an increase of the rigidity of the chain.

The constancy of  $T_g$  as the composition is varied in the range of high ethylene content agrees with the results

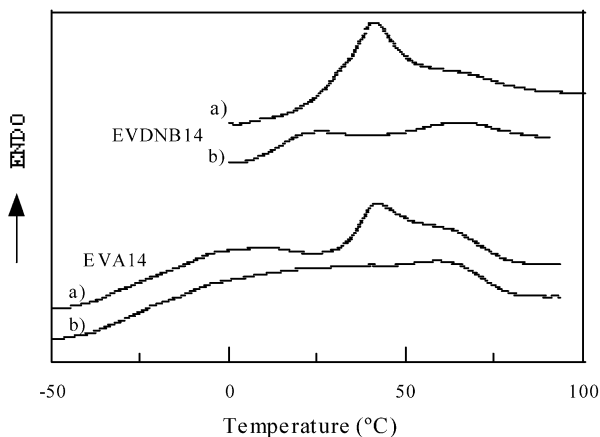


Fig. 12. DSC traces of EVA14 and EVDNB14 (heating rate  $20^\circ\text{C}/\text{min}$ ). (a) After annealing at room temperature for several days. (b) Second heating after rapid cooling from the melt.

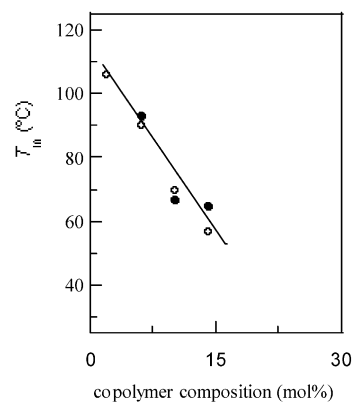


Fig. 13. Plot of melting temperature against mole percent of: ( $\square$ ) VA; ( $\bullet$ ) VDNB; for EVA and EVDNB copolymer samples.

Table 10  
Glass transition temperatures ( $T_g$ ), and melting temperatures ( $T_m$ ) of EVAL73, and EVALVDNB terpolymers

Sample code	Degree of transformation	$T_g$ (°C)	$T_m$ (°C)
EVAL73 <sup>a</sup>	0	55	188
EVALVDNB2	1.4	57	186
EVALVDNB7	7	59	163
EVALVDNB22	22	63	–
EVALVDNB72	72	96	–
EVALVDNB80	80	106	–
EVALVDNB93	93	114	–
EVALVDNB97	97	117	–

<sup>a</sup> From Aldrich.

reported in the literature [13,14]. This behaviour appears to be due to the fact that the branched olefinic chains are excluded entirely from the crystalline regions, therefore the composition of the amorphous phase is not the same as the overall composition of the polymer. As the acetate content increases the degree of crystallinity decreases, hence the amorphous copolymer phase is richer in ethylene, the composition of this phase is thus kept constant.

The melting peak is moved to lower temperatures as vinyl acetate and vinyl dinitrobenzoate molar fraction increases in the EVA and EVDNB copolymers. In Fig. 13 the melting points of these copolymers studied have been plotted against copolymer composition. EVA and EVDNB copolymer samples display identical melting temperature-composition relations from 0 to 14 mol% fraction of VA and VDNB. Beyond 50 mol% of VDNB the thermograms show no endotherm peak. Melting points of EVAL copolymers increase with the increase of hydroxyl groups in the copolymer, owing to the fact that they fit into the polyethylene crystal lattice.

### 3.4. EVALVDNB terpolymers

EVAL73 sample (73 mol% VAL) was partially esterified in order to get terpolymers of ethylene, vinyl dinitrobenzoate and vinyl alcohol. Table 10 shows the degree of transformation,  $T_g$ , and peak melting temperatures,  $T_m$ , of these terpolymers. An increase of about 65 °C is observed in  $T_g$  value when hydroxyl groups are completely replaced by vinyl dinitrobenzoate units. On the other hand,  $T_m$  values are lower for EVALVDNB terpolymers than for EVAL73 copolymer sample, as expected. From 10% of transformation the terpolymer samples no longer are crystalline.

## 4. Conclusions

The cyclic urea DMPU is an excellent solvent for EVAL copolymers having low and high alcohol content. The esterification of EVAL copolymers with 3,5-dinitrobenzoyl chloride in solution, using DMPU, shows full conversion and their esters display excellent solubility in it. On the other hand, NMP is not a solvent for the EVAL copolymers with low content of VAL, and the esterification of soluble copolymers is not complete. The glass transition temperature remains independent of the copolymer composition in the range of 2–14 mol% of the co-monomer, and increases above 50 mol%. The melting points of the copolymers decrease as the mol fraction of VDNB increases. EVALVDNB terpolymers with 27 mol% ethylene show that the substitution of hydroxyl groups for dinitrobenzoate units leads to an increase in  $T_g$  value, and that the crystallinity disappears from 10% of transformation.

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