

Cyclic Ureas as Solvents for Esterification of Poly(vinyl alcohol) and Vinyl Acetate-Vinyl Alcohol Copolymers with Acid Chlorides

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ABSTRACT: Poly(vinyl alcohol) (PVAL) and vinyl acetate-vinyl alcohol copolymers (VAVAL) were esterified with 3,5-dinitrobenzoyl chloride using the cyclic urea *N,N'*-dimethylpropyleneurea (1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone) (DMPU) as the solvent. Vinyl alcohol-vinyl-3,5-dinitrobenzoate copolymers (VALVDNB) and vinyl acetate-vinyl-3,5-dinitrobenzoate copolymers (VAVDNB) were obtained. High degrees of esterification were obtained when PVAL was esterified (86%). The degree of transformation was determined by $^1\text{H-NMR}$ as well as by chemical analysis, and the structure of the resulting polymers by means of IR spectroscopy and $^1\text{H-}$ and $^{13}\text{C-NMR}$. The microstructure of PVA, PVAL, VAVAL copolymers and VALVDNB copolymers were determined

from $^1\text{H-}$ and $^{13}\text{C-NMR}$ techniques. The sequence distributions for VAVAL copolymers prepared by base-catalyzed transesterification of PVA were blocky, while the distributions were close to random for VALVDNB copolymers obtained by esterification of PVAL. Thermal properties were studied by DSC. The T_g values of VAVAL, VALVDNB, and VAVDNB copolymers as a function of copolymer compositions were determined. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2509–2519, 2008

Key words: vinyl alcohol-vinyl-3,5-dinitrobenzoate copolymers; vinyl acetate-vinyl-3,5-dinitrobenzoate copolymers; 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone; thermal properties

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(vinyl acetate-co-vinyl alcohol) (VAVAL), and 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 to prepare poly(vinyl esters) has 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 with an acyl chloride often results in complications.

In esterification of PVAL it is important to obtain full substitution of hydroxyl groups to prepare the

required poly(vinyl esters). Esterification reactions under homogeneous conditions demand complete dissolution of PVAL and its esters in an appropriate solvent. Because of the stronger intermolecular and intramolecular hydrogen bonding PVAL can be dissolved only in water or in very polar solvents such as *N*-methyl-2-pyrrolidone (NMP) or dimethylsulfoxide (DMSO). Theoretically, 100% degree of esterification is possible only if PVAL can be dissolved in a nonaqueous solvent.

Esters of PVAL have been prepared using the interfacial Schotten–Baumann process.^{1,2} This interfacial esterification of PVAL with acyl chlorides does not give a complete substitution of hydroxyl groups and has not turned out to be a good method to prepare partially modified polymers. On the other hand, the esterification reaction of PVAL in homogeneous phase with acyl chlorides and NMP as a solvent also has been carried out.^{3,4} Using this method only partly substituted products with different degrees of esterification have been obtained.

In a previous paper⁵ we have esterified EVAL copolymers with acyl chlorides using the dipolar aprotic solvent *N,N'*-dimethylpropylene urea (DMPU) and the results obtained using DMPU and NMP are compared. We found that while with DMPU the esterification shows full conversion, with NMP using pyridine as catalyst the esterification is not complete.

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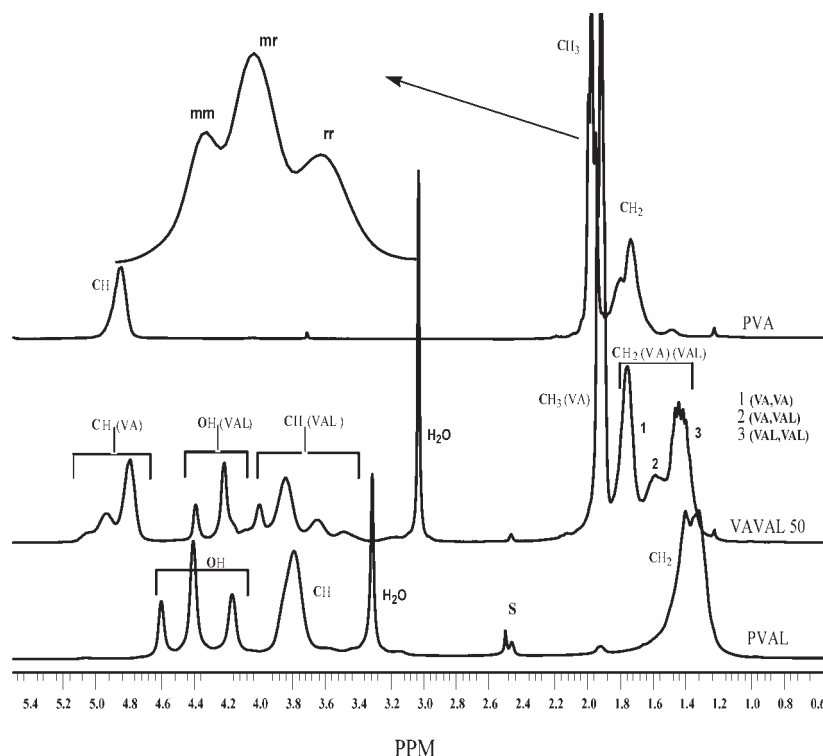


Figure 1 300-MHz ^1H -NMR spectra of PVA in CDCl_3 , PVAL, and VAVAL50 (50 mol % VAL) copolymer in $\text{Me}_2\text{SO}-d_6$, VAL, and VA denote the vinyl alcohol and vinyl acetate units, respectively.

In the present work, poly(vinyl esters) were synthesized through the homogeneous esterification of PVAL and VAVAL copolymers with 3,5-dinitrobenzoyl chloride in this dipolar aprotic solvent, the cyclic urea 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (*N,N'*-dymethylpropylene urea, DMPU). DMPU is an excellent polymer solvent and PVAL and VAVAL copolymers having low and high alcohol content, and their esters display excellent solubility in it. In this article we will describe some of our results regarding the use of DMPU to exemplify the utility of this solvent for poly(vinyl esters) synthesis from PVAL and vinyl alcohol copolymers with acyl chlorides.

EXPERIMENTAL

Materials

Commercially available poly(vinyl acetate) (PVA) ($M_w = 90,000$ g/mol) and poly(vinyl alcohol) (PVAL) ($M_w = 108,000$ g/mol; degree of hydrolyzation = 99.7 mol %) (Polysciences), 3,5-dinitrobenzoyl chloride (DNBC) (Fluka), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H) pyrimidinone (DMPU) (Fluka), pyridine (Fluka), 1-methyl-2-pyrrolidone (NMP) (Fluka) were used without further purification.

Synthesis of VAVAL copolymers

Copolymers of vinyl acetate and vinyl alcohol (VAVAL) were prepared by methoxide-catalyzed transesterification of PVA.^{6,7}

To a thermostated at 25°C and stirred solution of PVA in methanol (0.054M), a sodium-methylated so-

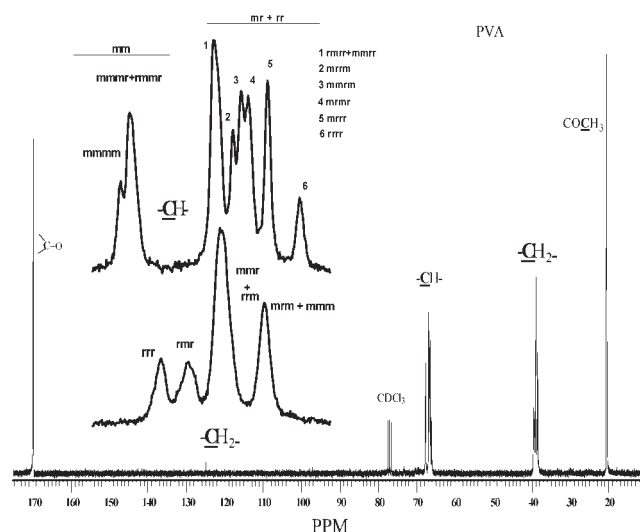


Figure 2 300-MHz ^{13}C -NMR spectrum of PVA in CDCl_3 , showing the amplified region of methylene and methine carbons.

TABLE I
Estimation of Tacticities of PVA

Method	Triads			Diads ^a	
	mm	mr	rr	m	r
Proton ^b	0.271	0.466	0.262	0.503	0.498
Carbon-13 ^c	0.23	0.77			

^a Calculated from triads.

^b Calculated from acetoxy methyl protons.

^c Calculated from methine carbon resonances.

lution was added (0.037M). The extent of hydrolysis was controlled by quenching the reaction after a specific time by neutralization with 1M aqueous acetic acid. The reaction mixture was concentrated by evaporation of methanol and the polymer precipitated by the appropriate precipitant (distilled water or acetone), washed and then reprecipitated (from methanol or aqueous solution), rewashed and finally dried under vacuum at 50°C.

Characterization of VAVAL copolymers

The IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrophotometer using polymer films on NaCl discs. The ¹H spectra were registered in Me₂SO-d₆ and spectra ¹³C-NMR in CD₃COCD₃, D₂O and mixtures of them, using a 300 MHz Brüker Avance DPX-300 spectrometer. DSC measurements were performed on a Polymer Laboratories DSC, connected to a cooling system and calibrated with different standards (indium, tin, lead, and zinc). The scanning rate used was 20°C min⁻¹ 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°C min⁻¹.

The degree of alcoholysis was determined by the saponification analysis of the samples as follows: the dried polymer was dissolved in an appropriate solvent (methanol, methanol/water, or water) (8.3 g/L), and then stirred at 60°C under reflux. Then a 0.1M sodium hydroxide solution was added slowly and

TABLE II
Tetrad Tacticity of PVA

Tetrads	Relative intensities	
	Calculated ^a	Observed ^b
rrr	0.156	0.124
rrm	0.134	0.145
mmr + rrm	0.497	0.482
mrm + mmm	0.213	0.248

^a The tetrads were calculated by using the Bernoullian parameter, *P_m* = 0.462.

^b Observed relative peak intensities.

TABLE III
Pentad Tacticity of PVA

Pentads	Relative intensities	
	Calculated ^a	Observed ^b
m m m m m	0.213	0.229
m m m m r		
r m m m r		
r m r r r	0.267	0.249
m m r r r		
m r r m m	0.062	0.081
m m r m m	0.106	0.105
m r m r r	0.124	0.120
m r r r r	0.191	0.147
r r r r r	0.084	0.067

^a Calculated using Bernoullian model with *P_m* = 0.462.

^b Observed relative peak intensities.

stirred for 2 h. The solution was then cooled at 22°C and titrated with 0.1M hydrochloric acid using phenolphthalein as indicator. The analysis was carried out in duplicate for each polymer. The modification extent was also determined by ¹H-NMR using either eqs. (1a) or (1b) or (1c)⁸:

$$VA = 2A_{CH_3}/3A_{CH_2} \quad (1a)$$

$$VA = A_{CH}(VA)/A_{CH}(VA) + A_{CH}(VAL) \quad (1b)$$

$$VA = A_{CH_3}/3A_{CH}(VA) + A_{CH}(VAL) \quad (1c)$$

where VA is the mol fraction of vinyl acetate, *A_{CH₃}*, *A_{CH₂}*, and *A_{CH}* represent the total peak area of the methyl, methylene and methine proton resonances, respectively. The results by both methods were in agreement.

Synthesis of vinyl alcohol-vinyl-3,5-dinitrobenzoate copolymers (VALVDNB) and vinyl acetate-vinyl-3,5-dinitrobenzoate copolymers (VAVDNB)

PVAL or VAVAL copolymers were dissolved in DMPU at 90°C, then a definite amount of DNBC, dissolved in DMPU, 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 period of time the modified polymer was isolated by precipitation using water as precipitant, then it was purified by reprecipitation using THF as solvent and methanol as precipitant, and finally dried in vacuum.

Characterization of VALVDNB and VAVDNB copolymers

The IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrophotometer using polymer films

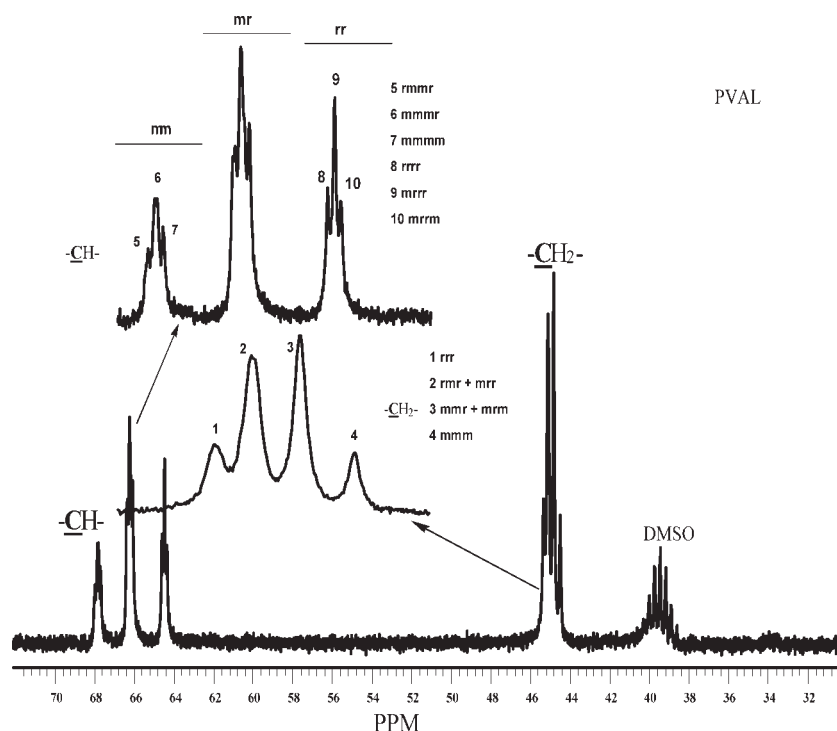


Figure 3 300-MHz ^{13}C -NMR spectrum of PVAL in $\text{Me}_2\text{SO}-d_6$, showing the amplified region of methine and methylene carbons.

on NaCl discs. The ^1H - and ^{13}C -NMR spectra were registered in $\text{Me}_2\text{SO}-d_6$, using a 300 MHz Brüker Avance DPX-300 spectrometer. DSC measurements were performed on a Polymer Laboratories DSC. Samples were scanned at $20^\circ\text{C min}^{-1}$ and the glass transition temperature (T_g) was taken as the initial onset of the change of the slope in the DSC curve. The degree of esterification was determined by ^1H -NMR.

RESULTS AND DISCUSSION

Base-catalyzed transesterification of poly(vinyl acetate) with methanol

Analysis by FTIR and NMR

PVA was converted to VAVAL copolymers by transesterification with methanol catalyzed by methoxide, the copolymers obtained were characterized by FTIR and NMR.

The IR spectra of the partly alcoholized PVA showed a carbonyl absorption at 1735 cm^{-1} , which corresponds to that of PVA, and the characteristic hydroxyl bands in the region $3700\text{--}3100\text{ cm}^{-1}$ confirm that transesterification had taken place.

Figure 1 shows the ^1H -NMR spectra of PVA, PVAL, and VAVAL copolymer 50 mol % VAL and the assignments of the peaks.⁸⁻¹⁶

Figure 2 shows the ^{13}C -NMR spectrum of PVA and the expansion of methylene and methine carbon

peaks where tetrad sequences and 8 of the 10 pentad sequences have been assigned.¹⁷⁻¹⁹

From acetoxy methyl protons and methine carbon resonances of PVA the triad tacticity can be determined.^{9-11,14,17,19} The results are given in Table I. The results indicate that our sample is atactic with $P_m = 0.462$ (the Bernoullian probability of forming a meso sequence in a growing polymer chain).

From methylene carbon resonances of PVA the tetrad distributions can be determined.¹⁹ The results are given in Table II. Table III gives the pentad distributions of PVA sample.

Figure 3 shows the ^{13}C -NMR spectrum of PVAL, the expansion of the methine carbon atom resonances where triad and pentad sequences have been assigned,^{20,21} and the amplified region of the methylene carbon atom resonances where tetrad sequences have been assigned.^{20,21} The fractions of triad tacticity of PVAL, which were calculated from the integrated methine carbon spectra, are summarized in Table IV. From triad data in Table IV, the parameter P_m is calculated, $P_m = 0.47$. In Table IV the observed tetrad tacticities from methylene carbon peaks are compared with theoretical values calculated from P_m . The tetrad distributions in PVAL can also be completely determined by using the following relationships of tetrads and triads: $\text{mnr} = 2(\text{mm}-\text{mmm})$, $\text{rnr} = \frac{1}{2}(\text{mr}-\text{mnr})$, $\text{mrm} = \frac{1}{2}(\text{mr}-\text{mrr})$, and $\text{mrr} = 2(\text{rr}-\text{rrr})$. The calculated results are also presented in Table IV.

TABLE IV
Triad and Tetrad Tacticity of PVAL

	Relative intensity		
	Observed ^a	Calculated ^b	Calculated ^c
Triad	¹³ C Methine resonances		
mm	0.22		
mr	0.50		
rr	0.28		
Tetrad	¹³ C Methylene resonances		
rrr	0.17	0.149	
rmr]	0.36	0.396	0.148
mrr]			0.222
mmr]	0.35	0.351	0.202
mrm]			0.138
mmm	0.12	0.104	

^a Observed relative peak intensities.

^b The tetrads were calculated by using the Bernoullian parameter, $P_m = 0.47$.

^c The tetrads were calculated by using the relationships of tetrads and triads.

Figure 4 shows the ¹³C-NMR spectra of two VAVAL samples with different VAL content, and the assignments of the lines are indicated on them.^{8,13,20,22–24} The spectra consist of four general carbon resonance lines. Two of these resonance lines are singlets at approximately 20 and 172 ppm and represent methyl and carbonyl (not shown) carbons, respectively, of acetyl groups. The remaining two broad, complex resonances are due to the methylene carbons (38–46 ppm) and methine carbons (63–72 ppm). The spectra shown differ in (a) relative inten-

sities of the three peaks in the methylene region, and (b) number and intensities of the lines in the methine carbon region. These differences can be explained in terms of variations in comonomer sequence distributions, chemical compositions, and branching.

The three methylene carbon lines can be used to quantitatively determine sequence distributions.^{13,22,25} The mole fractions of the dyad sequences can be calculated from integrated intensities of the three methylene lines. A quantitative description of sequence distribution and chemical composition is possible

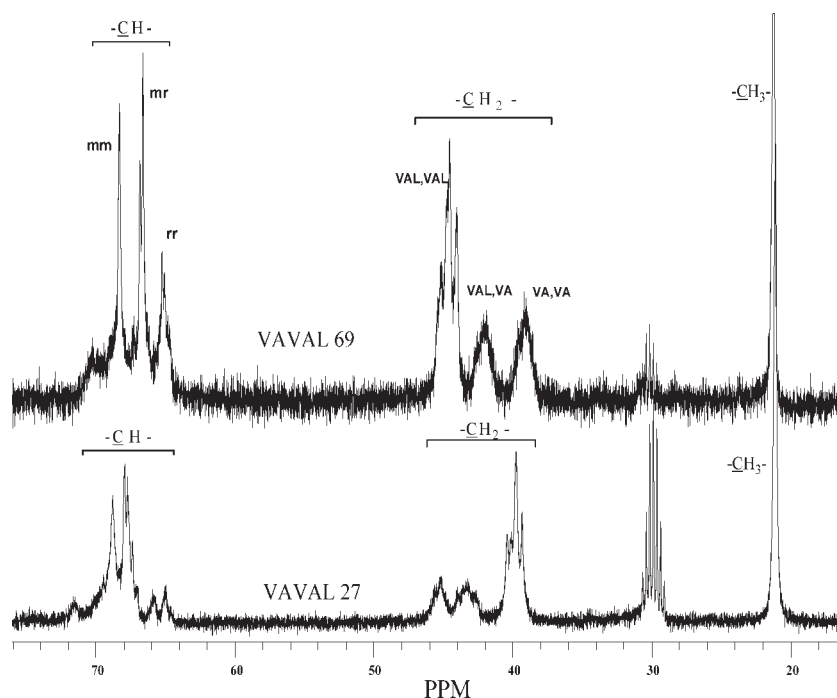


Figure 4 300-MHz ¹³C-NMR spectra of VAVAL copolymers (27 mol % VAL and 69 mol % VAL) in D₂O-CD₃COCD₃, VAL and VA denote the vinyl alcohol and vinyl acetate units, respectively.

TABLE V
Chemical Composition, Mole Fractions of Dyads, the Block Character, η , and the Mean Run Lengths, L_{VAL} , L_{VA} , of VAVAL Copolymers

Polymer	Composition (% mol)		Dyad (%)			VAL ^a (% mol)	η	L_{VAL}	L_{VA}
	VAL	VA	(VA, VA)	(VAL, VA)	(VAL, VAL)				
VAVAL 6	6	94	90	5	5	7	0.38	2.8	37.2
VAVAL 13	13	87	76	16	8	16	0.59	2.0	10.5
VAVAL 16	16	84	76	12	12	18	0.41	3.0	13.7
VAVAL 18	18	82	78	12	10	16	0.45	2.7	14.0
VAVAL 22	22	78	72	14	14	21	0.42	3.0	11.2
VAVAL 25	25	75	69	15	16	23	0.42	3.1	10.3
VAVAL 31	31	69	54	18	27	36	0.39	4.0	7.0
VAVAL 35	35	65	56	23	21	32	0.53	2.8	6.0
VAVAL 44	44	56	44	17	39	47	0.34	5.5	6.2
VAVAL 50	50	50	39	18	43	52	0.36	5.8	5.3
VAVAL 52	52	48	38	19	42	51	0.38	5.4	5.1
VAVAL 67	67	33	24	21	55	65	0.36	6.2	3.3
VAVAL 73	73	27	17	16	67	75	0.43	9.4	3.1
VAVAL 83	83	17	8	9	83	87	0.40	19.0	2.9
VAVAL 92	92	8	5	8	86	90	0.44	22.5	2.5

^a The values derived from the dyad data, for comparison.

by application of the following equations^{13,23,24,26} to the integrated areas of the three methylene carbon dyads:

$$VAL = (VAL, VAL) + (VAL, VA)/2 \quad (2)$$

$$VA = (VA, VA) + (VAL, VA)/2 \quad (3)$$

$$\eta = (VAL, VA)/2(VAL)(VA) \quad (4)$$

$$L_{VAL} = 2(VAL)/(VAL, VA) \quad (5)$$

$$L_{VA} = 2(VA)/(VAL, VA) \quad (6)$$

where VAL, mol fraction of vinyl alcohol units; VA, mol fraction of vinyl acetate units; L_{VAL} , number average run length of vinyl alcohol units; L_{VA} , number average run length of vinyl acetate units; η , block character of the copolymer.

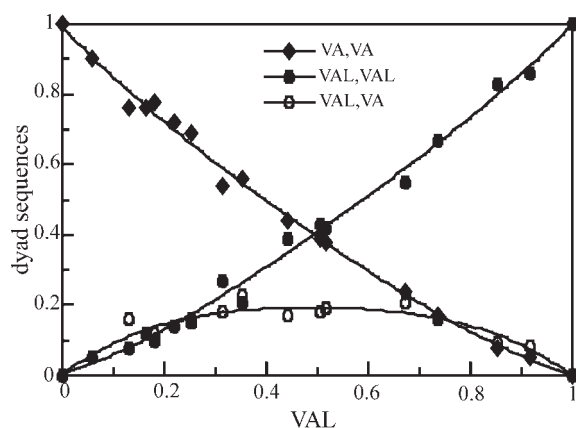


Figure 5 Plot of dyad fractions as function of the VAL content in the VAVAL copolymer.

The η value is a convenient guide to characterize a sequence distribution in binary copolymers; is a measure of departure from random character. It takes $0 \leq \eta < 1$ for blockier distribution; $\eta = 1$ for completely random cases; and $1 < \eta \leq 2$ for alternate-like cases.

The results of this analysis are shown in Table V. Figure 5 shows the mol fraction of dyads as a function of VAL content. From this Figure and from Table V it can be derived that the sequence distributions, for the VAVAL copolymers prepared by base-catalyzed transesterification, are highly blocky with $0.36 < \eta < 0.6$. The values of L_{VAL} and L_{VA} are similar to those reported in the literature.^{13,22}

Thermal properties

The thermal properties of the VAVAL copolymers were evaluated by DSC and the glass transition

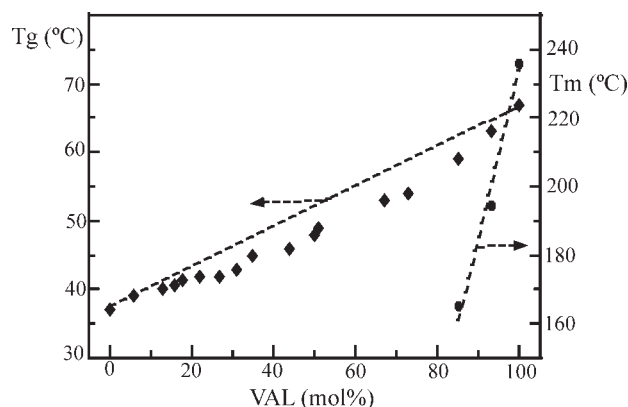


Figure 6 Glass transition temperatures and melting temperatures for VAVAL copolymers.

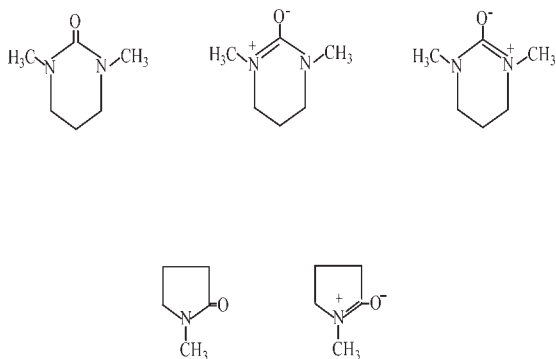
TABLE VI
Esterification of PVAL with 3,5-Dinitrobenzoyl Chloride

Run	Solvent	T (°C)	Time (h)	Degree of esterification (%) ¹ H NMR
1	DMPU	55	5	80
2	DMPU	55	7	82
3	DMPU	55	17	82
4	DMPU	55	120	81
5	DMPU	25	16	86
6	DMPU	25	160	86
7	NMP ^a	55	16	78
8	DMPU ^a	55	17	80

[PVAL] = 0.45M, [DNBC] = 0.56M.

^a Using pyridine as catalyst; 0.56M.

temperatures, as well as the melting temperatures are shown in Figure 6. The copolymer T_g s exhibit a negative deviation from linearity, that is attributed to lower barriers to main chain mobility than expected from simple additivity of the components. In VAVAL copolymers considerations of structural effects and hydrogen bonding must be taking into account to explain the behavior observed in Figure 6. The replacement of the bulky acetate side groups by hydroxyls leads to a higher chain mobility. On the other hand, in VAVAL copolymers T_g values are affected by hydrogen bonding. The increase of the content of hydroxyl groups results in an increase in hydrogen bonding, consequently, if increased hydrogen bonding alone is taken into account, an increase of the copolymer T_g above the predicted by additivity would be expected. Taking into account both effects, structural and intermolecular and intramolecular interactions, it is evident that changes in the rigidity of the polymer chains are unable to be counterbalanced by the increase of hydrogen bonding. The copolymer samples with a content of VAL units above 80 mol % are partially crystalline. The melting temperature is higher as the mol fraction of hydroxyl groups increases.



Scheme 1 Major resonance forms of DMPU and NMP.

Esterification of PVAL and VAVAL copolymers with 3,5-dinitrobenzoyl chloride

Chemical modification

PVAL and VAVAL copolymers were esterified with 3,5-dinitrobenzoyl chloride in a homogeneous medium by solution in DMPU.

The reaction conditions and the extent of esterification of VALVDNBs obtained are given in Table VI.

The results show that increasing the temperature higher than room temperature did not improve the degree of esterification. The influence of reaction time on degree of modification is negligible and a plateau (80–85%) is reached at 55°C in 5 h. The maximum extent of modification reached is 86%, the reason for this limit may be the steric hindrance due to β -keto ester groups incorporated in the chain. The great volume of these groups may make difficult or even prevent the reaction of alcoholic groups neighboring modified units. The use of pyridine as catalyst did not improve the degree of esterification. When comparing the result obtained using DMPU and NMP with pyridine as catalyst (according to the literature method⁴), the maximum extent of modification is obtained with DMPU alone.

DMPU and NMP are dipolar aprotic solvents with high dipole moments,^{27,28} attributed to the partial double bond character of its carbonyl carbon–nitrogen bond (Scheme 1). Comparison of the dipole moments and dielectric constants of both shows

TABLE VII
Physical Parameters of Solvents

Solvent	μ (D)	ϵ
DMPU ^a	4.23	36.1
NMP ^b	4.09	32.0

μ is the dipole moment and ϵ is the dielectric constant.

^a Ref. 26.

^b Ref. 27.

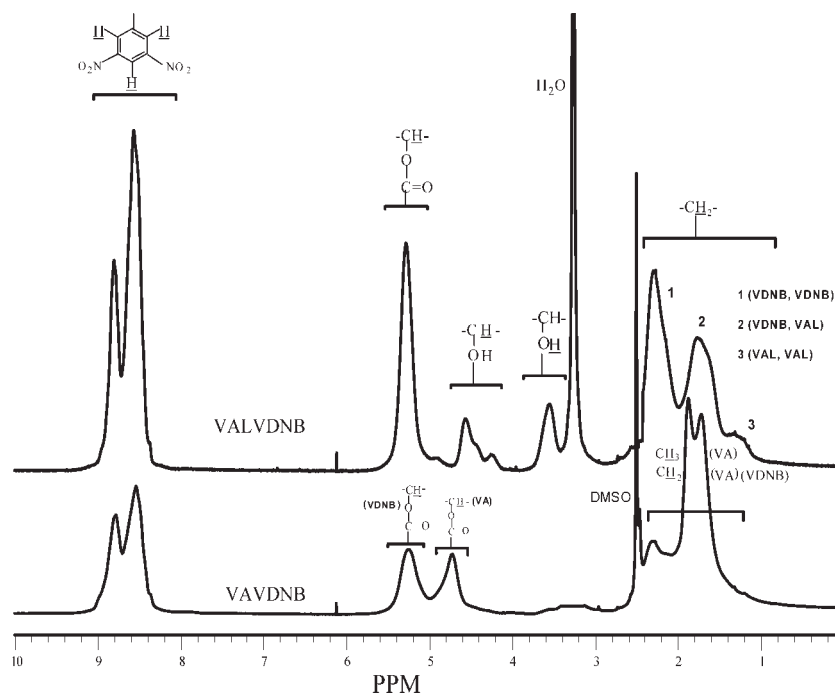


Figure 7 300-MHz ^1H -NMR spectra of VALVDNB (37 mol %VAL) and VAVDNB (48 mol %VDNB) copolymers in $\text{Me}_2\text{SO}-d_6$, VAL, VA, and VDNB denote the vinyl alcohol, vinyl acetate and vinyl dinitrobenzoate units, respectively.

DMPU has the highest dipole moment and dielectric constant (Table VII). 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.

Different PVAL : DNBC ratios were used to obtain several degrees of modification.

FTIR, ^1H -, and ^{13}C -NMR characterization

The structure of the resulting polymers was confirmed by IR, ^1H -, and ^{13}C -NMR spectroscopies.

The IR spectra of esterified PVAL and VAVAL copolymers with 3,5-dinitrobenzoyl chloride show a characteristic band of the pendant groups at 1730 cm^{-1} ($\text{C}=\text{O}$), 1546 cm^{-1} (NO_2 assym), and 1345 cm^{-1} (NO_2 sym).

The ^1H -NMR spectra of the same modified polymers are shown in Figure 7. The signals observed in the ^1H -NMR spectra of the modified PVAL at 8.5–8.9 ppm are due to the aromatic protons (3H) of the vinyl dinitrobenzoate (VDNB) units, the bands at 5.3 and 3.6 ppm are due to the methine ($-\text{CH}$) protons of the VDNB units and the VAL units, respectively, the signals at 4.3–4.6 ppm are due to the hydroxyl proton of the VAL units. The signals at 2.3, 1.8, and

TABLE VIII
Chemical Composition, Mole Fractions of Dyads, the Block Character, η , of VALVDNB Copolymers

Polymer	Composition (% mol)		Dyad (%)			η
	VAL	VDNB	(VDNB,VDNB)	(VAL,VDNB)	(VAL,VAL)	
VALVDNB 14	14	86	73	24	3	0.94
VALVDNB 16	16	84	65	33	2	1.11
VALVDNB 20	20	80	64	32	5	1.00
VALVDNB 22	22	78	58	36	6	0.99
VALVDNB 25	25	75	57	38	5	1.01
VALVDNB 30	30	70	49	43	8	1.02
VALVDNB 35	35	65	42	47	11	1.03
VALVDNB 37	37	63	38	50	12	1.07
VALVDNB 55	55	45	18	53	29	1.07
VALVDNB 78	78	22	4	38	58	1.10
VALVDNB 82	82	18	3	31	66	1.05

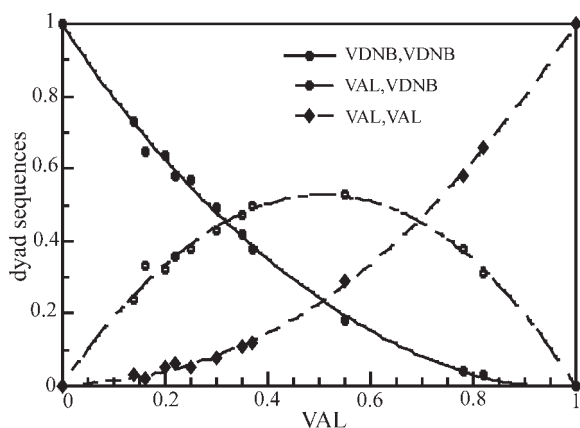


Figure 8 Plot of dyad fractions as function of the VAL content in the VDNB-VAL copolymer.

1.3 ppm are due to the methylene ($-\text{CH}_2$) protons of VDNB and VAL units, respectively, these lines can readily be assigned to the methylene protons in VDNB-VDNB, VDNB-VAL, and VAL-VAL dyads, as has previously been indicated for VAVAL copolymers. The composition of the VALVDNB copolymers was determined by comparing the peak at 4.3–4.6 ppm and the band at 5.3 ppm using the Eq. (7):

$$\text{VDNB} = A_{\text{aromatics}} / 3A_{\text{OH}}(\text{VAL}) + A_{\text{aromatics}} \quad (7)$$

where VDNB is the mol fraction of vinyl dinitrobenzoate, $A_{\text{aromatics}}$, and A_{OH} represent the total peak

area of the aromatic and hydroxyl proton resonances, respectively. From the methylene proton spectrum the sequence distribution in VALVDNB copolymers can be estimated, although it can merely be done in a qualitative manner because of the overlapping of the lines. The copolymer compositions and the mol fractions of dyads determined from the methine proton resonance and from the methylene proton resonance, respectively, for the various samples of VALVDNB copolymers prepared by esterification, are shown in Table VIII. Table VIII also shows the block character, η . The η values are between 0.94 and 1.11, which reflects a random distribution of monomeric units in the copolymers. Figure 8 shows the mol fraction of dyads as a function of VAL content. These results agree with data obtained from other studies.²⁹

Figure 9 shows the ^{13}C -NMR spectra of VALVDNB and VAVDNB copolymers. In the spectrum of modified PVAL, the carbonyl ester group signal can be seen at 162.2 ppm. The peaks around 122.3, 128.7, 132.8, and 148.3 ppm are assigned to the aromatic ring. The methine carbons, linked either to ester or hydroxyl groups give rise to broad signals between 63 and 75 ppm. In the region between 36 and 46 ppm the peaks corresponding to methylene carbons appear, although partially overshadowed by the multiplet of the solvent $\text{Me}_2\text{SO}-d_6$.

The signals observed in the ^1H -NMR spectra of the VAVDNB (Fig. 9) at 8.6–8.9 ppm are due to the

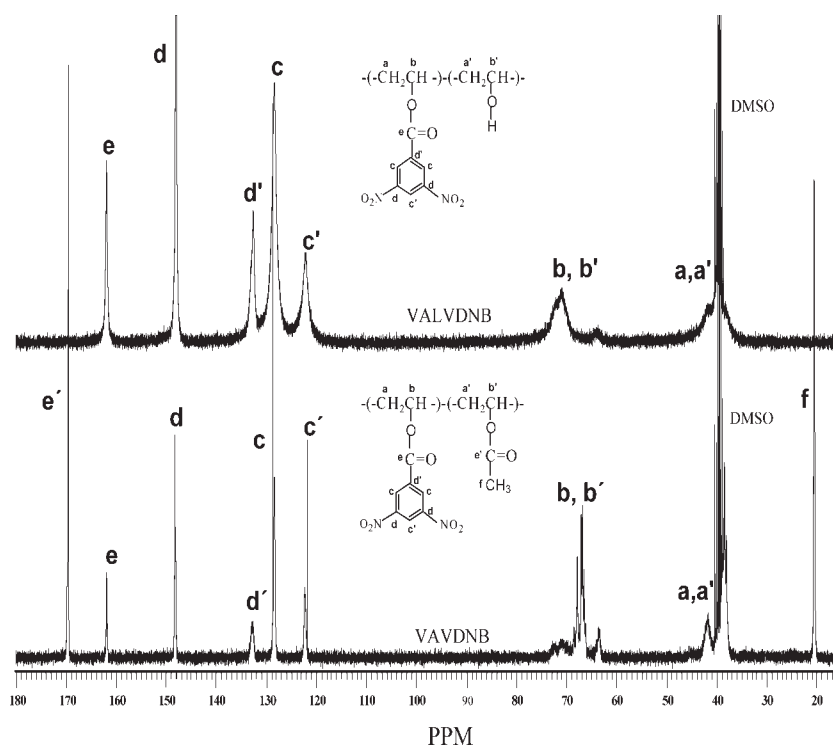


Figure 9 300-MHz ^{13}C -NMR spectra of VALVDNB (86 mol % VDNB) copolymer and VAVDNB (23 mol % VDNB) copolymer in $\text{Me}_2\text{SO}-d_6$.

aromatic protons (3H) of the VDNB units, the bands at 5.3 and 4.7 ppm are due to the methine ($-\text{CH}$) protons of the VDNB units and the VA units respectively, the signal at 1.9 ppm is due to the methyl ($-\text{CH}_3$) protons of VA, and the band at 1.7 ppm is due to the methylene ($-\text{CH}_2$) protons of VDNB and VA units. The copolymer composition was determined by comparing the peaks at 4.7 ppm and the band at 8.6–8.9 ppm using the Eq. (8):

$$\text{VDNB} = A_{\text{aromatics}} / 3[A_{\text{CH}}(\text{VA}) + A_{\text{CH}}(\text{VDNB})] \quad (8)$$

where VDNB is the mol fraction of vinyl dinitrobenzoate, $A_{\text{aromatics}}$ and A_{CH} represent the total peak area of the aromatic and methine proton resonances, respectively.

The composition was also determined by elemental analysis. The results by both methods were in agreement.

In the ^{13}C -NMR spectra of VAVDNB copolymer (Fig. 11), the acetate carbonyl ester group can be seen at 170.3 ppm, while the dinitrobenzoate carbonyl ester group appears at 162.4 ppm. The peaks around 148.8, 133.3, 129, and 122.8 ppm are assigned to the aromatic ring. The methine carbons, linked either to ester or hydroxyl groups give rise to broad signals between 63 and 74 ppm. In the region between 37.7 and 43.5 ppm the peaks corresponding to methylene carbons appear, although partially overshadowed by the multiplet of the solvent $\text{Me}_2\text{SO}-d_6$. The peak at 21 ppm is assigned to the methyl carbon resonance of the acetate group.

Thermal behavior

The T_g values of VALVDNB copolymers are showed in Figure 10. The T_g -composition behavior displays a negative deviation from linearity, as in the case of VAVAL copolymers. This result can be explained by

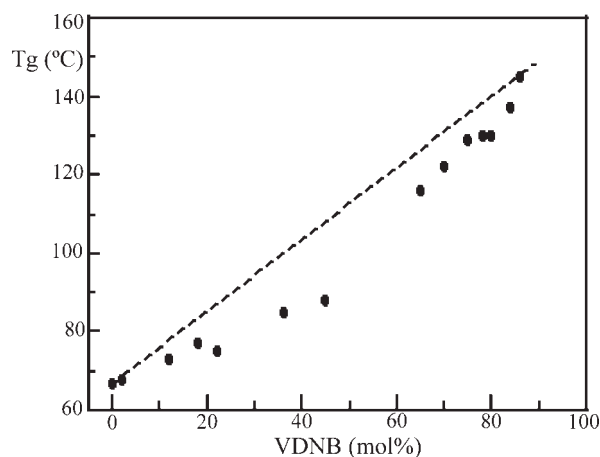


Figure 10 Glass transition temperatures for VALVDNB copolymers.

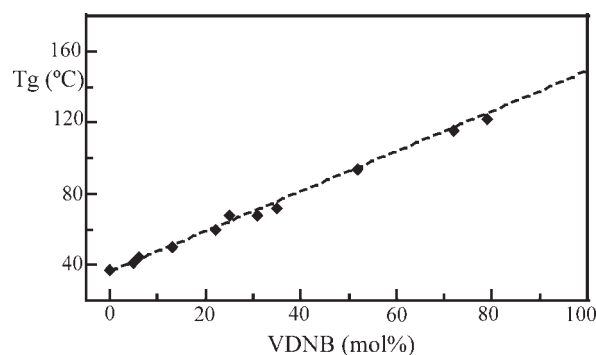


Figure 11 Glass transition temperatures for VAVDNB copolymers.

considering the influence of two factors, the substitution of hydroxyl groups by the bulky dinitrobenzoate units and hydrogen bonding. As the fraction of VDNB units in the copolymer decreases the rigidity of polymer chains is decreased. On the other hand, when the fraction of VAL units increases the number of hydrogen bonds increases, leading to increased values of T_g . Both opposite factors contribute to the observed T_g s, and it is clear that increase in hydrogen bonding in the copolymer samples is unable to balance the changes in chain mobility. The samples are not crystalline, and when comparing with VAVAL copolymers, it is observed that VALVDNB copolymer samples have higher T_g values due to the bulkier substituents that restrict rotation.

In Figure 11 T_g values of VAVDNB copolymers are plotted versus copolymer composition. It is seen that the values are located between those of the homopolymers, and that they change linearly with the VDNB content of the copolymers. Increased chain rigidity when the chains are substituted with bulky dinitrobenzoate substituents leads to higher T_g values.

CONCLUSIONS

The esterification of PVAL and VAVAL copolymers with 3,5-dinitrobenzoyl chloride in solution, using the cyclic urea DMPU, shows high conversion and their esters display excellent solubility in it. The modification extent of the esterification reactions can be determined using ^1H -NMR spectroscopy. The sequence distributions for VAVAL copolymers, obtained by base-catalyzed transesterification of PVA, are blocky, while a random sequence distribution is obtained for VALVDNB copolymers prepared by esterification of PVAL. The T_g values of VAVAL and VALVDNB copolymers display a negative deviation from linearity, while VAVDNB copolymer T_g s change linearly with

copolymer composition. VAVAL copolymers with a content of VAL units above 80 mol % are crystalline. On the other hand, VALVDNB copolymers are not crystalline.

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