

NOTE

New Adhesives Prepared from Vinyl Benzyl Chloride Copolymerization

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INTRODUCTION

Vinyl benzyl chloride (VBC) or chloromethylstyrene is known as a very versatile monomer. Numerous nucleophilic substitutions of the chlorine atom are possible, giving new monomers generally suitable to be polymerized or copolymerized.^{1,2} These substitution reactions were conducted with a great number of organic compounds, such as alcohols, amines, acids, sulfur derivatives or with bifunctional products, diols, and diamines providing divinyl benzyl derivatives. The applications of these dienic monomers are numerous, and many patents deal with the syntheses of optical lenses in which these monomers are used to prepare insoluble and flexible materials.²⁻⁴ Divinyl benzyl monomers have also been used as thermo setting resins that can be cured thermally. Poly(ether sulfone) terminated with the vinyl benzyl group have been synthesized by phase transfer catalysis,⁵ and the curing temperature of these oligomers depends on their molecular weight. The divinyl benzyl monomers were cured with or without adding a free radical initiator. Recently, some articles⁶⁻⁸ and patents^{3,4} have described the syntheses of *bis*(vinyl benzyl) ether or sulfide⁸ with their cure studies. They are few works dealing with the adhesive properties of VBC derivatives: *N*-vinyl benzyl imino diacetic acid has been described as a novel dental adhesive monomer⁹ and vinyl benzyl tetrasulfide has been used as monomer to prepare coating.¹⁰ In this article, we study the polymerization and copolymerization reaction of multi-divinyl benzyl derivatives, and we conduct a preliminary study of their mechanical and adhesive properties; with these multi-divinyl benzyl derivatives, we hope to obtain an increasing crosslink density of the adhesive.

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EXPERIMENTAL

Materials

VBC (Dow Chemical Corp., Midland, MI) was purified by vacuum distillation 50–55°C/0.5 mm Hg. The used initiators were:

1. Benzoyl peroxide (BP) purified after solubilization and precipitation with chloroform and methanol (1/1, v/v).
2. Azo *bis*-isobutyronitrile (AIBN; Fluka) recrystallized in a mixture with chloroform and methanol (1/1, v/v).
3. Cumyl hydroperoxide (HPC) (solution 50% in tBuOH) (Fluka).
4. *p*-Menthane hydroperoxide (solution 54%) (Solven-Chemie A.G.).
5. Methyl ethyl ketone hydroperoxide (MEKH; solution 50%) (Chimopar).
6. Lauroyl peroxide (LP) purified by recrystallization in chloroform (Fluka).

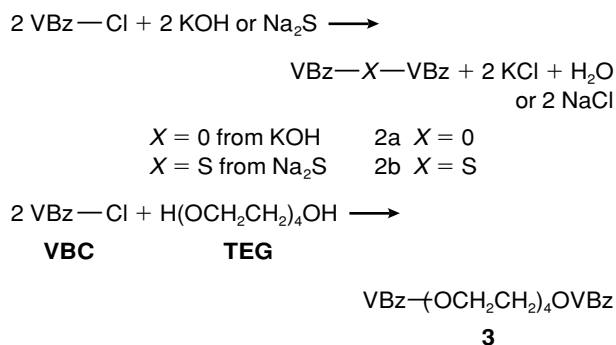
The catalysts for redox polymerization were cobalt stearate (CS) or cobalt naphthenate (CN) in toluene solution (Union Chimique Belge). 1–10 Phenantroline (FEN) was used for complexation of Fe²⁺ ions.

The other organic reactants or solvents—triethanolamine (TEA), tetraethylene glycol (TEG), and dioxane—are commercial and were used as received.

Methyl methacrylate (MMA) was distilled before use and methacrylic acid (AMA) (BASF) was used as received.

The polymer of MMA (PMMA) was prepared in bulk to a conversion of 30% and used in solution as a mixture of the starting monomer.

Infrared radiation (IR) spectra were recorded with



Scheme 1 Bifunctional derivatives synthesized from KOH, sodium sulfide, TEG, and VBC. VBz, vinyl benzyl radical.

a Fourier transform infrared 7PC Bio-Rad (Richmond, CA) apparatus. The ¹H-NMR spectra were recorded with a Varian apparatus EM 360 (frequency: 60 MHz) using CDCl₃ as solvent with tetramethylsilane as internal standard.

Elemental analyses were conducted at the Electro-technical Research Institute (Bucharest, Romania).

Mechanical testing was performed at the Laboratory of Corrosion Society S.A. Bucharest. Steel-laminated specimens were used for mechanical statical testing. Cylindrical butt-jointed specimens (surface of joint: ≈ 2 cm²) were used for the tensile strength test, whereas lap-jointed specimens were used for the shear test (surface of joint: 4 cm²).

Specimens were grit-blasted, the solvent washed, and then jointed with adhesive at 20°C for 24 h under 1 kgf/cm² pressure. Tensile strength was measured with a Shopper dynamometer at a strain rate of 5 mm/min and was calculated by means of 3–5 tests.

Syntheses of the Monomers

Monomers 1a–c TEA (0.1 mol) was charged in a 500-ml, three-necked, round-bottomed flask (fitted with a magnetic stirrer and reflux condenser), and 0.3 mol of potassium hydroxide (KOH) in dioxane was slowly added below 50°C. After the addition was complete, 0.3 mol of VBC, containing hydroquinone as inhibitor, was added for 30 min. After 3 h of stirring, the mixture was extracted with dichloromethane (3 × 100 mL), then washed with a 10% KOH solution to eliminate the inhibitor. The solution was dried with potassium carbonate, and the solvent was evaporated under vacuum.

Infrared spectra of this product showed peaks in the range of 3300–3500 cm⁻¹ corresponding to hydroxyl groups. The ¹H-NMR spectrum also showed peaks corresponding to the CH₂OH group in the range of 4.6–5

ppm. According to the goal of this work, it is not necessary to separate the components of the mixture 1a–c.

¹H-NMR (CDCl₃) δ ppm: CH₂N 3.6 (pattern); CH₂O 4.5 (pattern); CH = CH₂ 5.1–5.8 (dd); CH = CH₂ 6.4–6.8 (dd); aromatic protons 7.3–7.5 (pattern).

IR: OH (minor peak) 3300 cm⁻¹; CH = CH₂ 1630 cm⁻¹; CH₂O 1110 cm⁻¹.

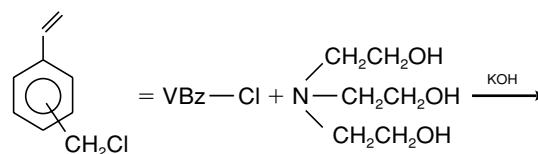
Monomers 2a,b (X = O; X = S) Monomers 2a,b were synthesized according to the procedure described by Muthiah and Mathias⁶ and Mathias and colleagues^{7,8} (Scheme 1).

The spectral characteristics of monomers 2a,b and elemental analyses were:

Monomer 2a—¹H-NMR (CDCl₃) δ ppm:—CH₂O 4.4 (s); CH = CH₂ 5–5.8 (dd); CH = CH₂ 6.1–6.3 (dd); aromatic protons 7.1 (pattern).

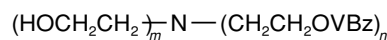
IR spectra: 1095 cm⁻¹ (ether function)
990–910 (vinyl bond).

Elemental analysis: C% cal 86.4, found 85.7; H% cal 7.2, found 7.



Vinyl benzyl chloride (VBC)

VBz = Vinyl benzyl radical

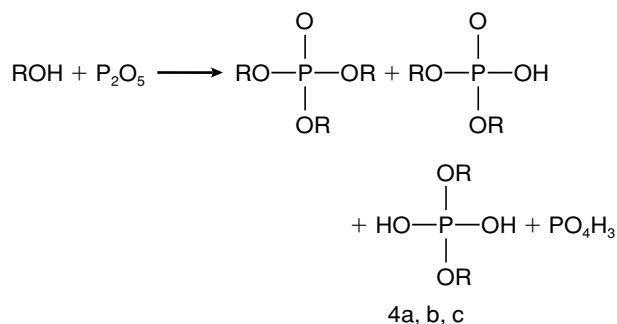


1a $m = 0$ $n = 3$

1b $m = 1$ $n = 2$

1c $m = 2$ $n = 1$

1a, b, c = R—OH



Scheme 2 Preparation of multifunctional derivatives of VBC.

Table I Copolymerization Reaction in Bulk at 70°C of Monomers 1a–c, 2a,b, and 3

Monomers	Initiator and Molar Proportion	Gelation Time ^a (mn)	Solidification Time ^b (h)
1a–c	AIBN 1%	14	4
1a–c	BP 1%	30	> 24
2a	BP 1%	No polymerization	
2a	BP 2%	> 3 h	
2b	BP 1%	No polymerization	
2b	BP 2%	No polymerization After 12 h	
2a	AIBN 1%	10	2
2b	AIBN 2%	10	2
2a	LP 1%	60	Gel after 24 h
2b	LP 1%	7	Gel after 24 h
3	AIBN 1%	10	5
3	BP 1%	25	Gel after 24 h
3 + MMA (15%)	BP 1%	20	5
3 + 15% solution of PMMA in MMA of conc. 30%	BP 1%	15	5

^a Gelation time of a system gives information about the maximum time of its processing. After this time, the viscosity is too high to permit any processing of the adhesive.

^b Solidification time is the minimum time after which the joint can be used. Values that are from 10 to 30 min for the gelation time and 24 h for the solidification time show a satisfactory reactivity of the systems.

Monomer 2b—¹H-NMR (CDCl₃) δ ppm: CH₂S 3.3 (s); CH = CH₂ 5–5.8 (dd); CH = CH₂ 6.3–6.9 (dd); aromatic protons 7.2 (pattern).

IR spectra: 990–910 (vinyl bond).

Elemental analysis: C% cal 81.2, found 80.5; H% cal 6.72, found 6.2.

The differences in elemental analyses between theoretical and found values are due to the non-distillation of these two monomers that could contain a minor proportion of impurities.

Monomer 3 This monomer was prepared by using the procedure described in ref. 11 (Scheme 1). In a three-necked flask (round-bottomed) equipped with a stirrer and reflux condenser, first TEG, dioxane, and KOH were charged at 60°C. Then, VBC containing hydroquinone as inhibitor was charged. The following ratios were used: VBC/TEG = 2/1 mol/mol, KOH/VBC = 2/1 mol/mol, dioxane/(VBC + TEG) = 1/3 v/v. After 16 h of stirring, the mixture was extracted with benzene, washed with 10% KOH solution, dried with K₂CO₃, and the solvent was evaporated under vacuum.

¹H-NMR (CDCl₃) δ ppm: OCH₂ CH₂O 3.8 (pattern); Ar

CH₂O 4.4 (singlet); CH = CH₂ 5–5.8 (dd); CH = CH₂ 6.3–6.9 (dd); aromatic protons 7.2 (m); CH₂O (ether function) 1100 cm⁻¹.

Monomer 4 Products were prepared by heating the mixture of monomers 1a–c synthesized in the following conditions: VBC/TEA = 2/1 (mol/mol); KOH/VBC = 2/1 (mol/mol); dioxane/VBC + TEA = 1/3 (v/v) with phosphorus pentoxide in anhydrous diethyl ether for 6 h. The reaction was conducted by refluxing the mixture in a round-bottomed flask with Dean-Stark apparatus.

Procedures used for preparations of the mixture were:

1. Monomer 4a 1a–c/diethyl ether = 1/1 (v/v); 1a–c/P₂O₅ = 2/1 (mol/mol)
2. Monomer 4b 1a–c/diethyl ether = 1/1 (v/v); 1a–c/P₂O₅ = 3/1 (mol/mol)
3. Monomer 4c 1a–c/diethyl ether = 1/1 (v/v); 1a–c/P₂O₅ = 5/1 (mol/mol).

Infrared spectra of the three samples showed that the absorption due to the hydroxyl group was low and depended on the ratio of starting monomers and phosphorus pentoxide. Due to the various proportions of these

Table II Copolymerization of Monomers 1a-c, 2a,b, 3, and 4 at 25°C

Run	Monomer	Initiators	Gelation Time (min)	Solidification Time (h)
1	1a-c	BP 1%	100	Remains gel after 24 h
2	1a-c	BP 1% + Fe ²⁺	160	Remains gel after 24 h
3	1a-c + 30% MMA	BP 1%	120	Remains gel after 24 h
4	1a-c + 15% MMA + 15% AMA	BP 3%	10	1.5
5	1a-c + 30% solution of PMMA in MMA of 30% conc.	BP 3%	10	Remains gel after 24 h
6	2a	MEKH 1% + CN 1%	240	48
7	2b	MEKH 1% + CN 1%	180	48
8	2a	MEKH 1% + CS 1%	180	48
9	2b	MEKH 1% + CS 1%	180	48
10	3	HPC 1% + CS 1%	> 120	24
11	3	HPC 1% + CS 1% + Fe ²⁺	> 120	24
12	3	HPC 1% + CN 1%	> 120	24
13	4a + 15% MMA	BP 5%	60	8
14	4b + 15% MMA	BP 5%	15	24
15	4c + 15% MMA	BP 5%	5	1.5
16	4c + 15% MMA	BP 1%	15	24
17	4c + 1a-c (3/1, g/g) + 15% MMA	BP 5%	5	0.5
18	4c + 3 (3/1, g/g)	HPC 1% + FEN 1% + Fe ²⁺	180	> 24
19	4c + 3 (3/1, g/g)	HPC 1% + FEN 1%	360	> 24
20	4c + 1a-c (1/1, g/g) + 15% MMA	BP 1%	20	3

products, we shall use the abbreviations 4a-c referring to the chosen experimental conditions (Scheme 2). MMA and PMMA were used for increasing initial viscosity of the system and AMA and FEN for transferring the ferrous cations in the organic phase.

Copolymerization of Monomers 1a-c, 2a,b, 3, and 4a-c

Experimental conditions for thermal at 70°C or redox reactions at 25°C are summarized in Tables I and II.

RESULTS AND DISCUSSION

The reactions of TEA with poly-VBC and a similar product the poly-chloromethylated styrene (result of the chloromethylation of styrene) have been briefly described,¹²⁻¹⁴ but the reaction of TEA with VBC monomer does not seem to have been studied. Tertiary amines (such as trialkylamines or pyridine) react with VBC to give an ammonium group by complexation of

the chloromethyl group that initiates a cationic polymerization.¹⁵ But in the chosen experimental reactions, TEA first reacts with KOH to give mainly an alcoholate function reacting by nucleophilic substitution with the chlorine atom of VBC. A careful examination of the IR spectra and the ¹H-NMR spectra showed that the reaction was not complete and that monomer 1 was in fact a mixture of mono-, di-, and trisubstituted products 1a-c. The hydroxyl groups in the IR spectrum are in the range of 3300-3500 cm⁻¹ and the -CH₂OH group in ¹H-NMR is observed at 4.6-5 ppm. To increase the purity of monomers 1a-c and to prepare pure monomer 1a with three vinyl benzyl units, several runs were conducted with formation of the alcoholate of TEA : KOH, and TEA in stoichiometric proportions were heated in a benzene solution; water was eliminated by means of a Dean-Stark trap for 8 h. The reaction was not complete and after reaction of VBC with this alcoholate, a similar product (a mixture of 1a-c) was obtained. Phosphorus pentoxide is known as a dehydration product for the preparation of anhydrides from acids, but the reaction with alcohols chiefly provided a mixture of phosphates¹⁶ besides minor proportions of alkenes or

Table III Mechanical Properties of Copolymers

Run	Composition of Adhesive	Stress at Break (kgf/cm ²)	
		Tensile Strength	Shear
1	1a-c + 15% MMA + 15% AMA + BP 3%	10.8	26.1
2	3 + HPC 1% + CN 1%	34.4	18.5
3	4c + 15% MMA + BP 1%	173.0	129.4
4	4c + 3 (3/1, g/g) + HPC 1% + FEN 1%	184.7	99.0
5	2a + MEKH 1% + CN 1%	42.0	36.0
6	2b + MEKH 1% + CN 1%	38.0	35.4
	Medium performance adhesives	20-50	20-50
	High-performance adhesives	> 100	> 100

Five test tubes were used with deviations of $\pm 15\%$. Essays have been conducted in the atmosphere and then, after 2 months, have been repeated five times with the same results. The metal surface has been prepared by sanding and, in $>90\%$ of essays, the breaking observed (by microscopy) was cohesive.

ethers. Therefore, the reaction of monomers 1a-c should give a complex mixture of phosphoric esters (Scheme 2), with several units of VBC monomer allowing a fast crosslinking reaction of the starting resins.

Two kinds of copolymerization reactions were conducted either with a radical initiator such as benzoyl peroxide or AIBN at 70°C or at 25°C using redox systems. Tertiary nitrogen from TEA can act as a reducing component in a redox system. The decomposition of the initiator is low at this temperature, and therefore either redox systems or an increased proportion of initiator have been used. The aim of this study was the preparation of reactive adhesives, and the time of gelation or solidification was the most important parameter. The main results are given in Tables I and II and from a practical point of view the best results (Table II) were obtained with mixtures 4, 7, 8, 10, 12, 13, 15, and 17.

The use of a high concentration of initiator increases the rate of the reaction, decreases the time of gel formation and, in some cases, decreases the duration of solidification.

For some of these systems, a tensile strength test or a shear test for the joint was conducted. Results are shown in Table III. Systems 2, 5, and 6 can be considered as medium performance adhesives, whereas systems 3 and 4 are good performance adhesives. In these cases, we have observed by microscopical analysis a cohesive breaking. This fact proves that the adhesive strength of the joint is superior to the value presented in Table III, and there is the possibility to enhance the cohesive strength by using structural materials. These adhesives are hydrophobic materials, so they have a better resistance to the chemical

hydrolysis in comparison with the polar adhesives (classical adhesives). The values of tensile and shear strength are similar to those found in high-performing adhesives that contain styrene or styrene derivatives.¹⁷ We suppose that the high performance is due to an increased density in crosslink of the adhesive or the presence of the phosphate functions that can react with the metallic surface.

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