

NOTE

Vinylbenzylchloride–Maleic Anhydride Copolymers: Flame Retardancy Properties and Relations Between Molecular Masses and Viscosity

INTRODUCTION

Chloromethylstyrene or vinylbenzylchloride (VBC) (pure para isomer or mixture of meta and para isomers, 60/40) was copolymerized with many comonomers such as acrylamide,¹ acrylonitrile,² buta-1,3-diene,³ divinylbenzene,⁴ methylmethacrylate,⁵ maleic anhydride (MAH),⁶ vinylacetate,⁷ ethylacrylate,⁷ styrene.⁷ The syntheses, nucleophilic substitutions (co)polymerization reactions of VBC, and chemical modifications of the resulting (co)polymers were reviewed.⁸ The numerous properties and applications are due to the ability of VBC to provide new monomers after nucleophilic substitutions of the chlorine atom, leaving the double bond undamaged.⁸ The new monomers are generally able to be polymerized or copolymerized. The reaction of triethyl phosphite with VBC provides vinylphosphonate diethyl ester synthesized in order to prepare copolymers with flame retardancy properties.^{9,10} As these properties of polyVBC (PVBC) have not been described, the present work deals with these characterizations as well as with those of copolymers of VBC-MAH (Scheme 1). The relations between intrinsic viscosity $[\eta]$ and molecular weights are also described.

EXPERIMENTAL

VBC (Dow Chemical Corp.) was purified by vacuum distillation (50–55°C/0.5 mmHg). MAH was twice recrystallized from chloroform, dried in vacuum at 30–35°C, and stored in a dry box. Toluene was distilled before use and azobisisobutyronitrile (AIBN) was recrystallized in a mixture of chloroform and methanol (1/1, v/v). Elemental analyses were performed at the Service Central d'Analyse (CNRS, Vernaison, France). The glass transition temperatures of the copolymers were recorded with a DSC 92 Setaram using a sample of 10–15 mg and a heating rate of 10°C/min.

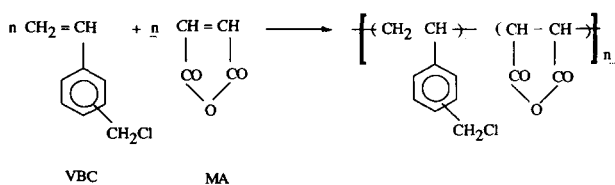
Dynamic thermogravimetric runs were studied using a Setaram G 70 thermal analyzer under a dry helium atmosphere at a flow rate of 50 mL/min. The initial weight of the sample was about 20 mg and the heating rate was

2.3°C/min. The molecular masses of copolymers were measured with a Knauer apparatus by using 10^3 – 10^5 Å columns, polystyrene standards, and tetrahydrofuran (THF) as solvent.

Viscosity measurements were carried out in a Schott-Gerate AVS automated viscosity-measuring system in THF at 25°C using an Ubbelohde type viscosimeter with low shear rate. The temperature was controlled to within ± 0.01 °C and the error of the flow times was 0.01%. The viscosity data were extrapolated to zero concentration (Fig. 1) to obtain values for intrinsic viscosity $[\eta]$ according to the Huggins equation $\eta_{sp}/c = [\eta] + k'[\eta]^2c$, where c is the polymer concentration, η_{sp}/c is the reduced viscosity, and k' is the Huggins constant. The flame retardancy properties of copolymers were characterized using a modified oxygen index method (MOI).¹¹

Preparations of Copolymer of VBC with MAH

Copolymerization reactions were carried out in solution in toluene using various proportions of VBC and MAH. The total molar concentrations of monomer and AIBN were, respectively, 2.0 mol/L and 3×10^{-2} mol/L for runs 1–6 (copolymers F_1 – F_6). The molar concentrations of AIBN were modified for runs 1'–7' (copolymers $F_{1'}$ – $F_{7'}$), respectively, 0.3, 0.6, 1, 2, 3, 5, and 10 au) $\times 10^{-2}$ mol/L and constant molar proportions of 10/90 for VBC/MAH were maintained. The copolymers were recovered by filtration, purified by washing several times with methanol/acetone (90/10, v/v) for extraction of low molecular mass products, and then were dried in vacuum at 35°C during 24 h. The characterizations of these two kinds of copolymers are given in Tables I and II.



Scheme 1 Synthesis route of VBC-MAH copolymers.

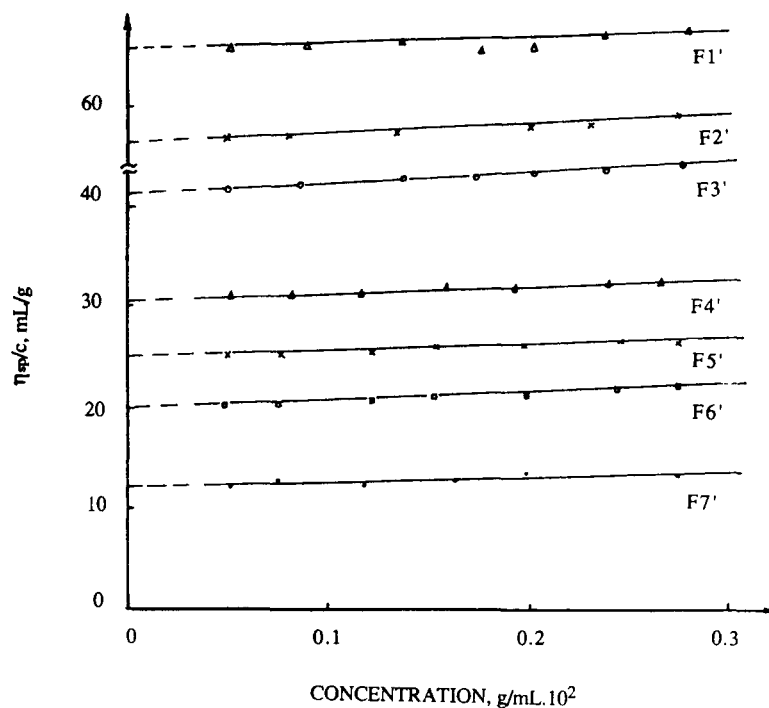


Figure 1 Variation of the reduced viscosity η_{sp}/c as a function of the concentration c for VBC-MAH copolymer fractions $F_1'-F_7'$.

Table I Copolymerization Conditions of VBC with MAH

Copolymer	VBC/MAH Composition (mol/mol)		Yield (wt %)	T_g ($^{\circ}\text{C}$)	MOI
	Feed	Copolymer			
F_1	10/90	45.02/54.98	15	181	43
F_2	20/80	46.20/53.80	31	180	44
F_3	30/70	47.48/52.52	40	169	44
F_4	50/50	52.0/48.0	58	166	45
F_5	70/30	57.24/42.76	60	154	46
F_6	90/10	70.17/29.83	62	145	48
PVBC	100	—	—	73	45

Table II Various Values for VBC-MAH Copolymers $F_1'-F_7'$

Fraction	F_1'	F_2'	F_3'	F_4'	F_5'	F_6'	F_7'
AIBN (10^2 mol/L)	0.3	0.6	1.0	2.0	3.0	5.0	10.0
$[\eta]$ (mL/g)	71	53	42	31	25	20	13
\bar{M}_n	107,000	80,000	51,000	28,000	18,000	8,500	1,800
\bar{M}_w	173,000	110,000	77,000	38,000	26,000	10,000	4,200
$I = \bar{M}_w/\bar{M}_n$	1.61	1.37	1.51	1.36	1.45	1.18	2.29

Copolymers were reprecipitated twice.

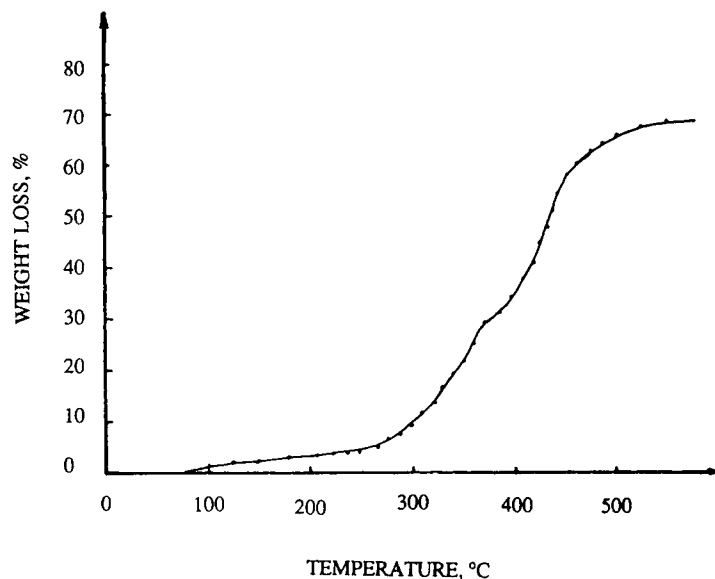


Figure 2 Dynamic thermogravimetric curve for VBCMAH copolymer F_1 heated in helium.

RESULTS AND DISCUSSION

The results presented in the Table I show that the percentages of VBC in the copolymers increased from 45 to 70% with the molar fraction of VBC in the initial feed mixture. These percentages of incorporated VBC are in agreement with the known reactivity ratios of the copo-

lymerization of VBC-MAH that are, respectively, 0.974 and 0.00 according to Bauduin et al.¹² or 1.08 and 0.02 according to Umarova.⁶ For copolymerizations F_1 - F_3 the molar fraction of MAH in the feed composition $f_{MAH} > 0.7$ was obtained (Table I) from the chlorine content, $F_{MAH} > 0.5$ (F_{MAH} is the molar fraction of MAH in the copolymer). Similar results were given by Umarova⁶ for

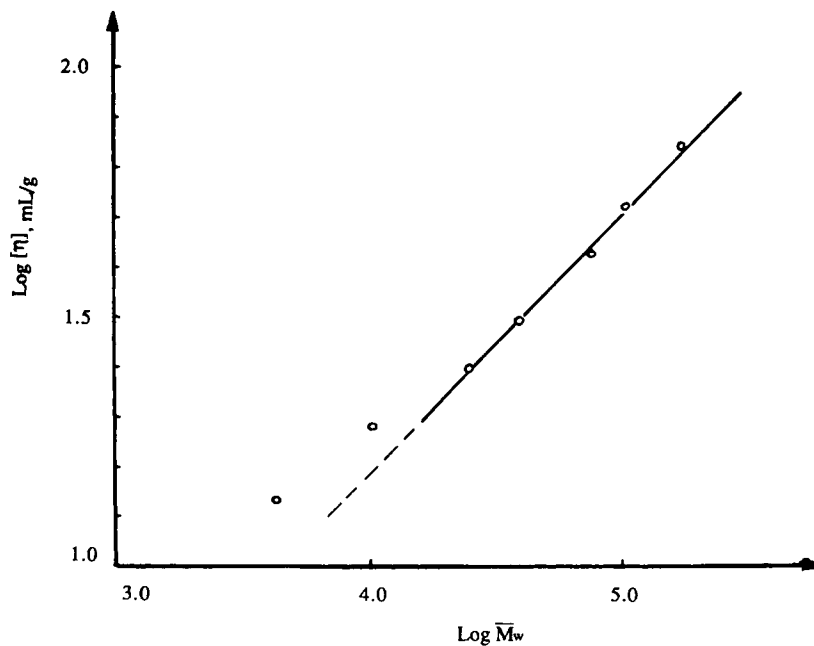


Figure 3 Graph of $\log [\eta]$ as a function of $\log \bar{M}_w$ for VBC-MAH copolymer fractions F_1 - F_7 . The solvent was THF at 25°C.

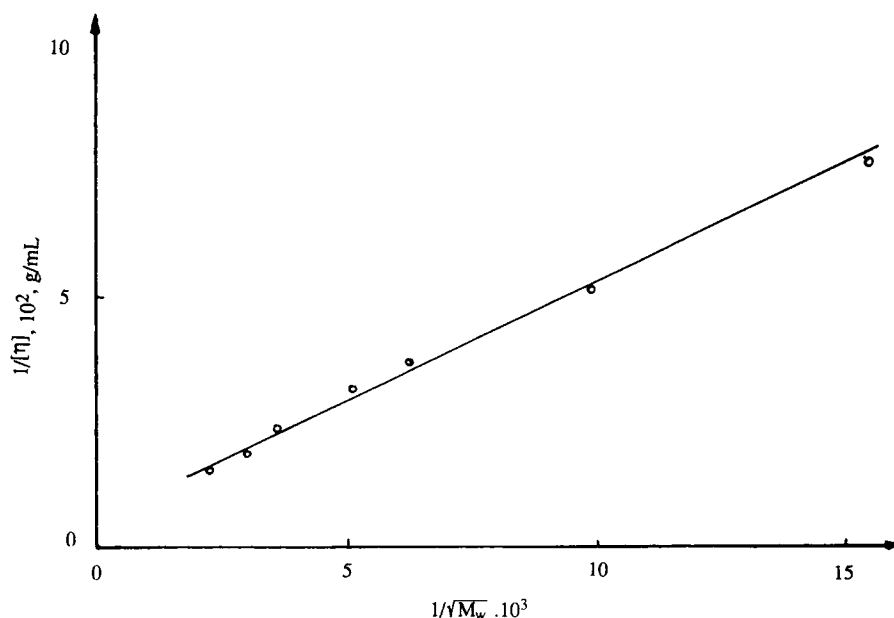


Figure 4 Graph of $[\eta]^{-1}$ as a function of $M^{-1/2}$ for VBC-MAH copolymer fractions F_1 – F_7 . The solvent was THF at 25°C.

VBC-MAH copolymer and for other copolymers of MAH.^{13,14} It has been suggested¹³ that the hydrogen atom of MAH is likely to be extracted by a radical, and a short branch of MAH can occur.

The values of the glass transition temperatures decrease with the increase of incorporated VBC due to the relatively low value of those of PVBC prepared from the mixture of meta and para monomers (73°C).

The thermogravimetric analysis of sample F_1 in programmed heating runs indicates that the thermal degradation occurs in two steps in the range 275–370°C and 390–485°C (Fig. 2). The global weight loss at 560°C is close to 69% of the initial weight.

The values of MOI for the VBC-MAH copolymers (F_1 – F_6) are given in Table I and seem independent of the variation of percentage of incorporated VBC. The MOI value for PVBC is 45 and the range of MOI for the six copolymers is 44–48. The chloromethyl group introduced on the aromatic nucleus increases the value of MOI comparatively to those of polystyrene¹¹ which is 19 and to those of phosphonated polystyrene¹¹ (MOI 27–35) and of partially chloromethoxyphosphonated polystyrenes¹⁵ (MOI 18–46).

The values of intrinsic viscosity $[\eta]$, number average molecular weight, \bar{M}_n , weight average molecular weight, \bar{M}_w , and polymolecularity index $I = \bar{M}_w/\bar{M}_n$ for the copolymers F_1 – F_7 prepared with a constant molar ratio of 10/90 VBC/MAH are given in Table II.

Plots of $\log [\eta]$ versus $\log \bar{M}_w$ in THF is shown in Figure 3. For low molecular weight samples, a deviation of the intrinsic viscosity is observed from the straight line that gives the representation of the Mark-Houwink-Sakurada (MHS) equation obtained with the polymer sample of higher molecular weights. For molecular

weights $\bar{M}_w > 10^4$, the equation ($[\eta]$ in mL/g solvent THF) at 25°C was $[\eta] = 0.103 \bar{M}_w^{0.54}$.

A new relation,^{16,17} between the intrinsic viscosity and molecular weight of a macromolecule, in the region in which the MHS equation is not valid, was proposed

$$\frac{1}{[\eta]} = -A_2 + \frac{A_1}{\bar{M}_w^{1/2}}$$

This semiempirical relation is closely related to the Stockmayer-Fixman equation¹⁸ and provides a good straight line between $[\eta]^{-1}$ and $\bar{M}_w^{-1/2}$ in a molecular weight region from 2×10^3 to 1×10^5 for VBC/MAH copolymers (Fig. 4). The values of A_1 and A_2 are +4.757 and 0.0065, respectively.

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