

Heterogeneous Nucleating Agents for Crystallization of Vinylidene Chloride-Vinyl Chloride Copolymers

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Synopsis

Nineteen compounds are described that are effective heterogeneous nucleating agents for the crystallization of poly(vinylidene chloride-vinyl chloride) copolymers containing 7-13% vinyl chloride. Most of the compounds are relatively high-melting organic nitrogen heterocyclics. The more effective ones raise the polymer freezing points about 20-40°C using a prescribed thermal history.

INTRODUCTION

Copolymers of poly(vinylidene chloride) containing more than about 45% vinyl chloride may crystallize.¹ The rate and amount of crystallization and the resulting polymer morphology depend upon the amounts of comonomers present, the thermal history, orientation, and the presence of additives such as plasticizers. Other additives behaving as heterogeneous nucleating agents may also affect the crystallization process. Copolymeric crystalline nucleating agents containing poly(vinylidene chloride) have been previously reported to be effective in promoting the crystallization of vinylidene chloride copolymers, especially those containing copolymerized acrylonitrile.^{2,3} This paper reports a number of nonpolymeric compounds that are effective heterogeneous nucleating agents for the crystallization of vinylidene chloride copolymers containing 7-13% copolymerized vinyl chloride.^{4,5}

The copolymers used are described in Table I. Under the experimental melting and freezing conditions described below, they may supercool about 45° to 100°C. The experimental procedure for determining the efficacy of added compounds as nucleating agents involves measuring the reduction in supercooling in the presence of small amounts of the compounds. The higher the freezing point of the mixture, the better the compound is considered to be as a nucleating agent.

EXPERIMENTAL

The finely powdered copolymers were intimately mixed with 0.5-1.0 wt-% of the nucleating agents by dry blending. The mixtures were heated in aluminum sample pans in a Perkin-Elmer differential scanning calorimeter,

TABLE I
 Copolymers Used

Copolymer	Composition, %		Melting point, ^c °C	Maximum temperature, ^d °C	Relative viscosity ^e
	VeCl ₂ ^a	ViCl ^b			
A	92-93	7-8	161, 181	197	1.74
B	89-91	9-11 ^f	161, 171	197	1.49
C	89-91	9-11 ^g	148, 164	187	1.53
D	87-88	12-13	154	187	1.53

^a Vinylidene chloride.

^b Vinyl chloride.

^c Endothermic peaks observed at a scanning rate of 20°C/min. Values are uncorrected for temperature.

^d Maximum temperature during melting-freezing cycle.

^e 2% Solution in *o*-dichlorobenzene at 140°C.

^f Also contains approximately 2% dinonyl adipate plasticizer.

^g Also contains approximately 12-15% stabilizers and plasticizers.

Model DSC-1, at 20°C/min from 97°C to a maximum temperature of 187°C or 197°C (Table I). The mixtures were cooled *immediately* at 20°C/min until crystallization was complete as evidenced by an exotherm. The peak of the exotherm, the point of intersection of tangents to the curve, was recorded as the freezing point, T_p .

RESULTS AND DISCUSSION

The thermal instability of vinylidene chloride copolymers is well known,¹ and it determined to a great extent the maximum temperature used in the melt-freeze cycles. Most likely these temperatures were not sufficiently high to remove all past history from the samples, but they were selected to give minimal decomposition under the temperature scanning rates used. The thermal procedure employed imparted a reproducible thermal history and freezing point to each sample. The concentrations of nucleating agents employed are somewhat higher than commonly employed in heterogeneous nucleation. The higher concentrations were used for screening of large numbers of compounds and to overcome the often negative effects encountered when plasticizers and stabilizers are present.

The 19 best nucleating agents found from approximately 1000 compounds screened are listed in Table II roughly in order of overall effectiveness. The better nucleating agents reduce the supercooling approximately 20-40°C. All but one, 2-hydroxy-3-naphthoic acid hydrazide, are organonitrogen heterocyclic compounds and/or their salts. Their melting points are relatively high: 16 melt at over 200°C; and eight, at over 300°C. Only 6- and 7-nitroindazole melt in the range of the maximum heating temperatures. Polymer C, which contained a relatively large amount of added plasticizers and stabilizers, responded well to nucleation. The last seven compounds were considered to be ineffective in polymer D. None

TABLE II
Freezing Points of Nucleated Copolymers

Compound	T_p , °C			
	A	Copolymers		
		B	C	D
	114	76	79	<65
6-Nitrobenzimidazole, sodium salt	134	111	120	99
Trichloromelamine	133	117	109	95
Melamine	132	116	105	97
6-Nitroindazole	134	112	101	95
5,6-Dichlorobenzimidazole	132	106	97	98
2-Phenylbenzimidazole	131	111	95	95
2-Hydroxy-3-naphthoic acid hydrazide	128	112	97	93
Lithium isonicotinate	133	109	92	85
5,6-Dimethylbenzimidazole	126	108	99	85
2,5,6-Trimethylbenzimidazole	126	105	90	91
5-Chloro-2-methylbenzimidazole	127	107	94	83
6-Nitrobenzimidazole	134	101	102	66
2-Benzimidazolylurea	127	118	95	<65
4-Nitroindazole	132	113	89	<65
2-Hydroxybenzimidazole	133	98	100	<65
5-Nitroindazole	133	113	85	<65
Potassium isonicotinate	130	104	90	<65
7-Nitroindazole	134	97	82	<65
Sodium <i>p</i> -pyridylhydroxymethanesulfonate	126	86	92	<65

of the compounds was an effective nucleating agent in a copolymer consisting of 78% vinylidene chloride and 22% vinyl chloride.

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References

1. R. A. Wessling and F. G. Edwards, in *Encyclopedia of Polymer Science and Technology*, Vol. 14, H. F. Mark and N. G. Gaylord, Eds., Wiley, New York, 1971, pp. 540-79.
2. G. Messwarb, K. T. Schotte, and W. Dummer (to Farbwerke Hoechst Aktiengesellschaft), U.S. Pat. 3,108,017 (Oct. 22, 1963).
3. H. G. Hahn and N. A. Lefevre (to Dow Chemical Company), U.S. Pat. 3,240,742 (March 15, 1966).
4. H. N. Beck, H. D. Ledbetter, and J. A. Schmitt (to Dow Chemical Company), U.S. Pat. 3,769,269 (Oct. 30, 1973).
5. H. N. Beck, H. D. Ledbetter, and J. A. Schmitt (to Dow Chemical Company), U.S. Pat. 3,793,265 (Feb. 19, 1974).

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