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Grafting of Poly(Methyl Methacrylate) onto Poly(Vinyl Chloride) through Benzodithioate Groups

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ABSTRACT

The synthesis and the characterization of poly(methyl methacrylate) (PMMA) grafted to poly(vinyl chloride) (PVC) through benzodithioate groups are studied. Unlike results generally obtained with conventional free-radical initiators for systems involving PVC and MMA, high conversions, and grafting efficiencies are achieved with azobisisobutyronitrile. The paper describes the synthesis of p-vinylbenzodithioate-containing PVC and the dependence of the characteristics of PVC-g-PMMA on the composition of the reaction mixture. Characterization of the graft copolymers includes UV and IR spectroscopy, GPC, and microstructure analysis by removal of PMMA side chains by aminolysis of dithioesters groups. Intrinsic viscosity, glass transition temperature, and thermal sensitivity were investigated to confirm the grafted nature of the copolymer.

INTRODUCTION

Work devoted to block and graft copolymers has boomed spectacularly during the last decades. Extensive studies on various aspects of graft polymers have appeared in the specialized literature, and patent publications have multiplied. Relevant information and numerous references on different facets of this polymer chemistry can be obtained from monographs on the subject [1, 2].

Poly(vinyl chloride) (PVC) is one of the most studied synthetic polymers for grafting with various vinyl monomers in order to improve its impact and tensile strengths [3] as well as its UV and thermal stability [4]. Uses of such copolymers are very diverse, from coatings to adhesives, from bulletproof jackets to inflammable materials. Labile chlorine atoms provide potential sites for grafting, and different methods can be used for initiation: electron beam [5], radiochemistry [6], high-energy irradiation [7], and ionic [8] or free-radical initiation [9], among others. Grafting of methyl methacrylate (MMA) to the PVC backbone by free-radical initiation has received the most attention [10].

Redox initiation involves reducing compounds of transition metals and halogen atoms in the polymer, avoids (or limits) homopolymerization, and leads to high grafting efficiency [11]. However, while good results have been obtained with MMA and several chlorinated polymers [12], such initiation has been unsuccessful with PVC [13]. With conventional free-radical initiators, the rate of grafting is often slow, and PVC has been found to be a retarder for the free-radical polymerization of MMA [14]. Hence, conversion and grafting efficiency are generally low [10], and reproducibility is uncertain. Some attempts have been made, therefore, to introduce onto PVC more reactive groups than labile chlorine atoms [15].

In a previous paper we described the substitution of chlorine atoms of PVC by benzodithioate groups without dehydrochloration [16]. This represents the direct application to PVC of the reaction of dithiocarboxylate quaternary ammonium salts with alkyl halides [17] and introduces polymerizable sites onto the polymer backbone. Here we describe free-radical grafting of PMMA to PVC that bears *p*-vinylbenzodithioate moieties (VBDT) and the characterization of the resulting copolymers.

EXPERIMENTAL

Modification of PVC by *p*-Vinylbenzodithioate Salt

The scheme described in Ref. 16 is applied to the substitution of chlorine atoms of PVC by VBDT groups (Fig. 1). A solution of PVC (low molecular weight, Aldrich, Ref. 18.333.97) and tetramethylammonium *p*-vinylbenzodithioate (1) (15 mol% referred to PVC) in THF is

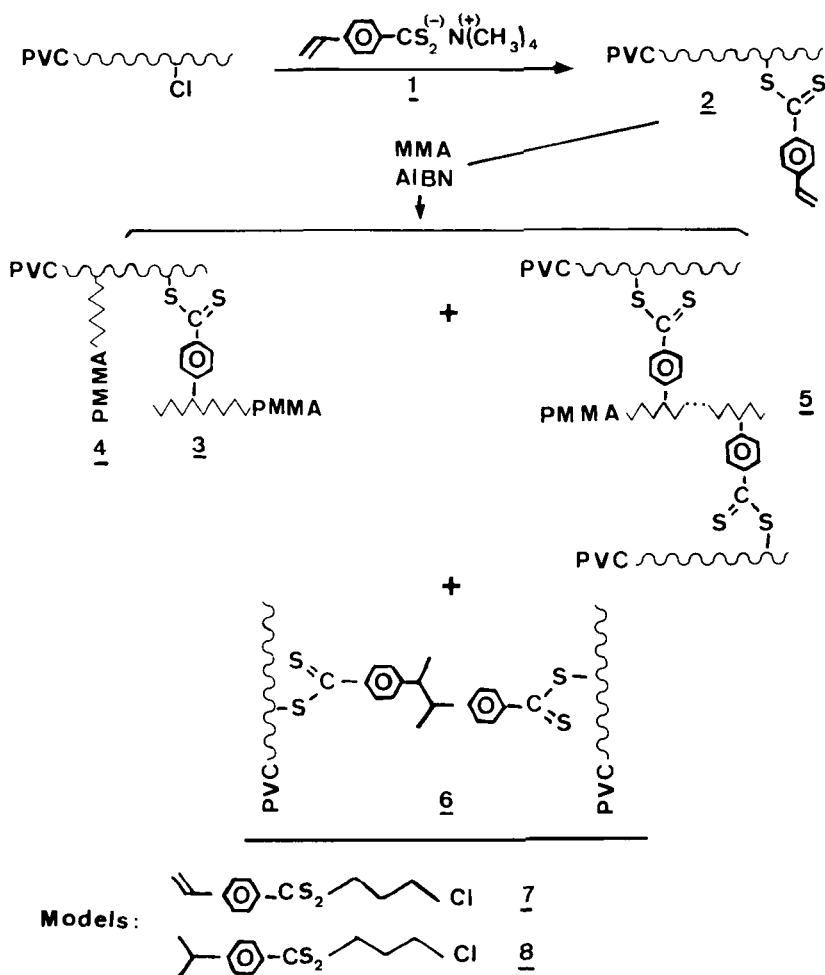


FIG. 1. Synthesis of PVC-g-PMMA through VBDT groups.

stirred at 15°C for the time needed to give the required content of VBDT groups on the PVC. The reaction is fast at the beginning, but then the rate drops to a steady value. This phenomenon is attributed to the particular lability of some of the chlorine atoms, estimated to amount to 0.25% by extrapolating the kinetic curve to origin (Fig. 2). Once past this first phase, the rate constant for substitution of chlorine atoms by p-vinylbenzodithioate at 15°C is calculated to be $k_{15} = 2.14 \times 10^{-3} \text{ L}/(\text{mol}\cdot\text{h})$ (correlation coefficient 0.992). Thanks to its p-vinyl group, Compound 1 is slightly more reactive than its unsub-

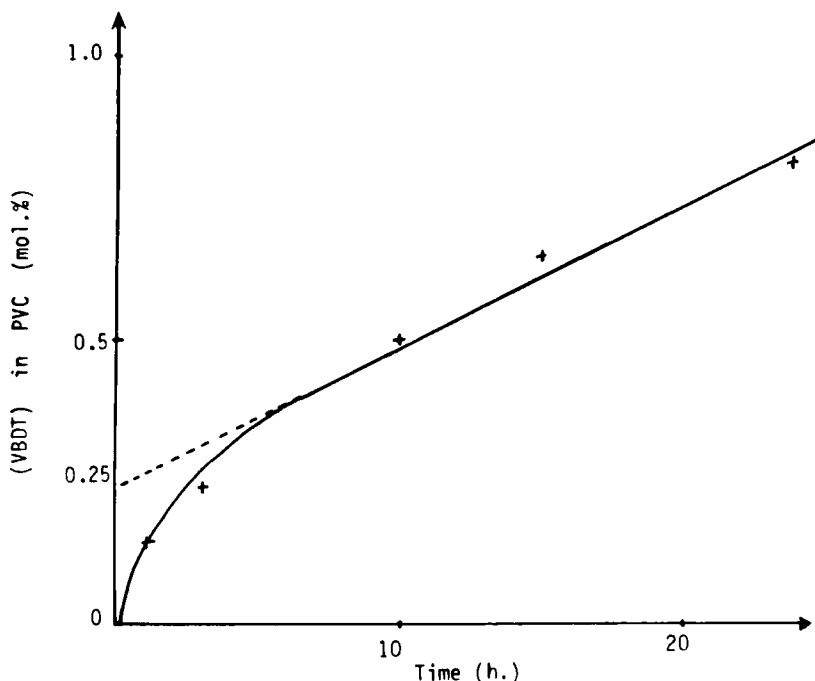


FIG. 2. Kinetics of the substitution of chlorine atoms of PVC by *p*-vinylbenzodithioate (VBDT). Temperature, 15°C; solvent, THF; [PVC] = 0.775 mol/L; [Compound 1] = 0.116 mol/L.

stituted homologs ($k_{20} = 6.25 \times 10^{-4}$ L/(mol·h) [16]). During the reaction, no gelation or precipitation occurs, which would be an indication of interaction between vinyl groups. The modified PVC is poured into methanol and purified by the usual dissolution-precipitation procedure with THF-methanol. Elemental analysis (either % Cl or % C) is not precise enough to allow reliable determination of VBDT contents of less than 1%. However, previous work [16] has shown that the spectroscopic data for higher contents (obtained by measuring the absorbance of the thiocarbonyl groups on the polymer based on a dithioester model) fit the analysis well, thus indicating no noticeable influence of the polymer chain on the absorbance of the thiocarbonyl group. Hence, the VBDT content is determined by UV spectroscopy at 332 nm (in THF) based on the absorbance of a model of the moiety 2, *p*-vinylbenzodithioic acid 3-chloropropyl ester (7). Experimental results for the preparation of VBDT-containing PVC are reported in Table 1.

TABLE 1. Substitution of Chlorine Atoms of PVC by p-Vinylbenzodithioate Groups^a

PVC no.	Reaction time, h	[VBDT], mol%	\bar{M}_n (GPC) $\times 10^{-3}$	\bar{M}_w (GPC) $\times 10^{-3}$	Average number of (VBDT) groups per macromolecule
1	1	0.14	32	78	0.7
2	3	0.24	32	84	1.2
3	7	0.42	28	79	1.8
4	10	0.50	26	86	2.0
5	15	0.65	24	82	2.4
6	24	0.82	25	90	3.2

^a[PVC] = 0.755 mol/L, [Compound 1] = 0.116 mol/L, solvent THF, temperature 15°C, initial PVC $\bar{M}_n = 35\,000$, $\bar{M}_w = 84\,000$.

Grafting of PMMA on PVC Backbone

We have limited our study to the effect of the reaction time and of the ratio of MMA to VBDT-containing PVC on the composition of the grafted copolymers.

Synthesis of PVC-g-PMMA

Solutions in THF of PVC bearing the Group 2 and MMA in various proportions were heated for several hours at 65°C under nitrogen with azobisisobutyronitrile (AIBN) as free-radical initiator. The initial overall concentrations of vinyl groups (including both MMA and pendent styryl groups on PVC) was 0.682 mol/L and that of AIBN, 0.020 mol/L (3% vs monomers) for all runs. After cooling, the solution was poured into methanol and filtered.

In conventional graft copolymerization, the separation of homopolymer from the grafted copolymer is often difficult, and sophisticated methods have been developed [18, 19]. However, in the case of PMMA and PVC-g-PMMA, the solubilities are generally different enough to allow purification of the copolymer by extraction with a good solvent for the homopolymer [20]. Soluble or crosslinked copolymers were stirred with hot benzene (60°C) in order to extract the homo-PMMA. After centrifugation, undissolved residue was separated, washed twice with fresh benzene, dissolved (or swollen to a gel) in THF, and precipitated by pentane addition. Pouring of a benzene solution into pentane led to precipitation of homo-PMMA. The treatment can be repeated to check the absence of polymer in the benzene solution, but generally a single treatment was sufficient to remove all the homopolymer, which rarely exceeded 10% of the initial MMA. The absence of chlo-

rine in the PMMA fraction demonstrated the efficiency of the extraction. Above ~75% PMMA in PVC-g-PMMA, this procedure is no longer applicable because the copolymer begins to be soluble in benzene. In this case we separated the homo- and copolymer by chromatography of a solution of crude polymer in THF-benzene (30-70) on a column of silica gel (Merck 70-230 mesh) according to a process derived from one previously described by Horii and Ikada for poly(styrene)-g-poly(vinyl acetate) [21].

Methods of Analysis

UV and visible spectra were recorded on a UV-vis Varian DMS 100 spectrometer.

IR analyses were done on a Nicolet 5 DX. Polymer samples were ground and pressed into KBr pellets.

^1H NMR spectra were recorded on a 60-MHz Varian FT 80A. All data are given in δ (ppm), with TMS as reference and CDCl_3 as solvent.

GPC determinations were carried out on a Waters instrument with two sets of columns. Conditions: for \bar{M}_n over 20 000, two columns, Shodex A 803 and A 805, 60 cm each. For \bar{M}_n under 20 000, five columns, Styragel, $1 \times 1\ 000 \text{ \AA}$, $3 \times 500 \text{ \AA}$, $1 \times 100 \text{ \AA}$. Solutions: 30 mg polymer in 5 mL THF at 25°C . Detection by differential refractometer and UV analyzer at 254 nm.

T_g and thermal stability were studied on a Du Pont 990 analyzer.

Samples of polymer: 2 mg in sealed capsules under nitrogen. Heating rate: $20^\circ\text{C}/\text{min}$ for T_g determination.

Melting points were determined with a hot-stage microscope Reichert Thermovar.

Characteristics of Model Compounds

3-Chloropropyl p-Vinylbenzodithioate (7). Red oil prepared from Compound 1 and 1-bromo-3-chloropropane according to Ref. 17 (yield 70%), bp (760) = 186°C (dec). ^1H NMR: 2.25 (m, 2H), CH_2 ; 3.60 (m, 4H), S-CH_2 and $\text{CH}_2\text{-Cl}$; 5.65 and 6.85 (3H), vinyl group; 7.40 and 8.15 (A_2B_2 , 4H), phenyl protons. UV-vis (THF): $\lambda_{\text{max}} = 287.7$ ($\log \epsilon = 3.90$), $\lambda_{\text{max}} = 332.2$ ($\log \epsilon = 4.29$), $\lambda_{\text{max}} = 506.0$ ($\log \epsilon = 2.25$); (CHCl_3): $\lambda_{\text{max}} = 284.7$ ($\log \epsilon = 3.85$), $\lambda_{\text{max}} = 332.7$ ($\log \epsilon = 4.26$), $\lambda_{\text{max}} = 499.9$ ($\log \epsilon = 2.25$).

3-Chloropropyl p-Isopropylbenzodithioate (8). Red oil prepared from trimethylbenzylammonium p-isopropylbenzodithioate and 1-bromo-3-chloropropane according to Ref. 17 (yield 65%), bp (760) = 158°C (dec). ^1H NMR: 1.30 (d, 6H), $(\text{CH}_3)_2$; 2.20 (m, 2H),

CH_2 ; 2.95 (m, 1H), CH isopropyl; 3.55 (m, 4H), CH_2CS and CH_2Cl ; 7.35 and 8.10 (5 H), aromatic protons. UV-vis (THF): $\lambda_{\text{max}} = 314.0$ nm ($\log \epsilon = 4.09$), 499.9 nm ($\log \epsilon = 1.97$).

p-Isopropylbenzothiopiperamide (13). Synthesized from Compound 8 and piperidine in benzene; recrystallized from pentane (yield 80%): yellow needles, mp = 58.1 C. ^1H NMR: 1.20 (d, 6H) and 2.90 (m, 1H), isopropyl group; 1.65 (6H), 3.45 (2H) and 4.40 (2H); piperidinyl group; 7.25 (s, 4H), phenyl group. UV-vis (CH_3CN): $\lambda_{\text{max}} = 230.2$ nm ($\log \epsilon = 4.12$), 249.2 nm ($\log \epsilon = 4.18$), 283.4 nm (4.11), 375.2 ($\log \epsilon = 2.48$).

RESULTS AND DISCUSSION

The introduction of pendent VBTD groups into PVC leads to several possibilities of reactions during free-radical grafting (Fig. 1). Beside the usual grafting by chain transfer from a growing polymer chain of PMMA to the PVC backbone (leading to Structure 4), copolymerization of MMA with the vinyl group of the VBTD moieties 2 occurs, leading to Structure 3 and possibly to crosslinked copolymers. Homopolymeric impurities are removed during the purification of the copolymer. Yields of the different structures depend on the experimental conditions and the starting compounds, especially the VBTD content of the PVC.

Determination of the Composition of PVC-g-PMMA

Free-radical initiation does not affect the dithioester function, and many homo- and copolymers of polymerizable dithioesters have been synthesized by this route [22]. The presence of a thiocarbonyl group as a connection between the PVC backbone and some PMMA sidechains allows UV determination of the percentage of PMMA in the copolymer. Analyses were carried out in THF at 314 nm according to the absorption maximum of the 3-chloropropyl ester of p-isopropylbenzodithioic acid (8) chosen as a model of Unit 3. All soluble PVC-g-PMMA samples exhibit the characteristic band at 314 nm.

When the copolymer was crosslinked, IR was used instead of UV. A typical IR spectrum of a (PVC-g-PMMA) (31% PMMA) is given in Fig. 3. Strong absorbances at 1730 and 1715 cm^{-1} are related to the ester group of the methacrylate moieties, while the band at 613 cm^{-1} is attributed to the C-Cl bond in grafted-PVC samples [23]. Quantitative measurements of the absorbances at 1730 and 1715 cm^{-1} and comparison of the absorbances at 1730 and 615 cm^{-1} with use of the corresponding calibration plots allow the determination of the per-

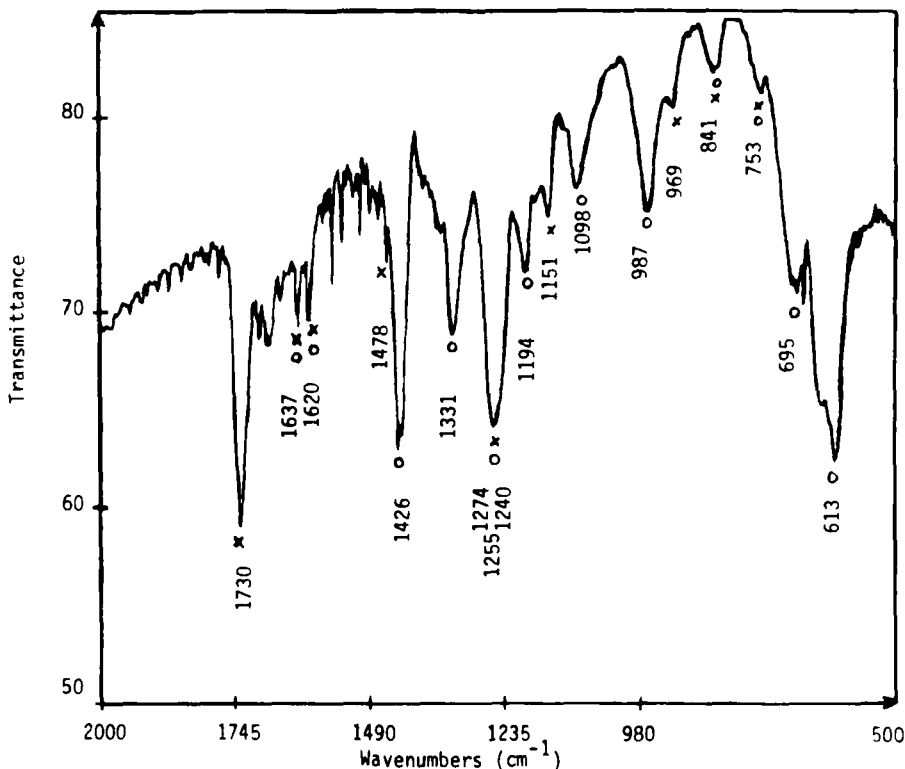


FIG. 3. IR spectrum of a 48 mol% PMMA-containing PVC-g-PMMA in KBr: (x) band related to PMMA, (o) band related to PVC.

centage of PMMA in the copolymers. A fair correlation between the UV and IR methods was found for soluble copolymers, and we have used this latter method as the single analysis of crosslinked copolymers. In addition, compositions were checked by elemental analysis (% C, % Cl) and fit the spectroscopic data well (Table 2).

Influence of the Reaction Time

The variation of the PMMA content in PVC-g-PMMA with reaction time was studied for a 0.42% VBBDT-containing PVC with 45 mol% MMA in the initial mixture (Fig. 4). No further increase in grafting was noted after 7 h (85% grafted PMMA) under our conditions.

The homo-PMMA is estimated to be 5%. After separation and puri-

TABLE 2. Analysis of PVC-g-PMMA

PVC no. ^e	PVC (mol%) in PVC-g- PMMA		IR ^a	Homo-PMMA ^b	% Conversion ^c	G ^d	Elemental analysis			
	UV ^a	IR ^a					Calculated		Found	
							C%	Cl%	C%	Cl%
6	-	12 ^f		14	54	0.46	38.60	42.95	39.41	41.76
5	-	27 ^f		16	67	0.63	45.93	40.03	44.95	39.38
4	24.0	21		~5	86	0.91	41.83	42.57	-	-
1	46.0	44		~5	87	0.81	47.70	30.24	48.19	29.86
2	53.5	52		~5	78	0.90	51.30	25.98	50.92	25.02
3	74.0	72		~5	93	0.93	52.16	14.72	54.09	13.95

^aUV data \pm 0.5%; IR \pm 1%.^bmol% vs charged MMA.^c% Conversion = (grafted PMMA + homo-PMMA) $\left(\frac{100}{\text{charged MMA}} \right)$.^dG = grafting efficiency = $\frac{\text{grafted PMMA}}{\text{converted PMMA}}$.^eSee Table 1.^fCrosslinked copolymer.

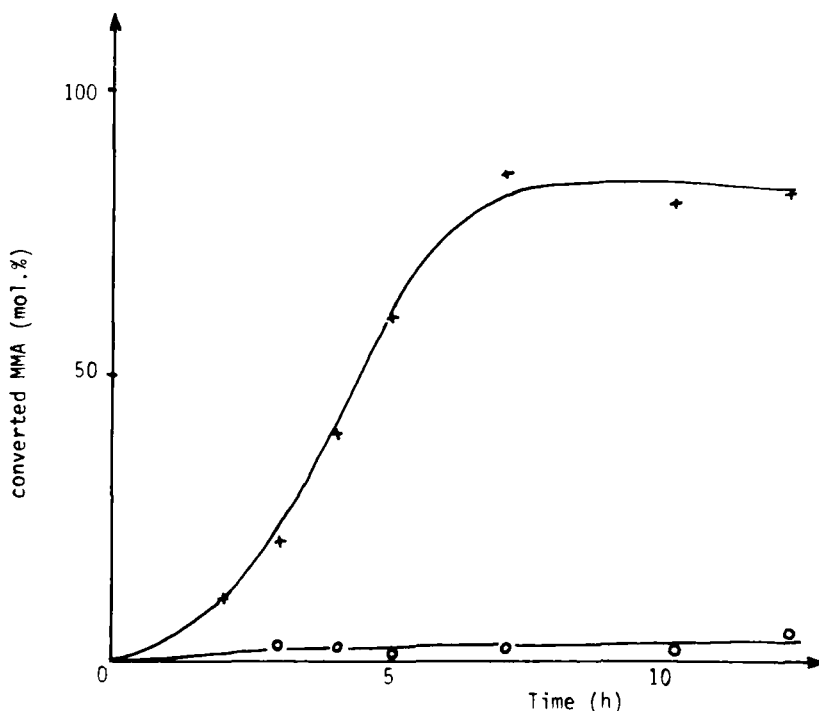


FIG. 4. Kinetics of conversion of MMA: (+) grafted PMMA on PVC, (o) homo-PMMA.

fication, a soluble sample of PVC-g-PMMA was heated for a further 3 h at 65° in THF with additional AIBN and remained wholly soluble, thus indicating that all vinyl groups of the VBTD moieties have reacted or are not accessible for further reaction. Thus, in the subsequent study all runs were carried out for 7 h.

Effect of the MMA/PVC Ratio on the Grafting

Figure 5 shows the PMMA content in PVC-g-PMMA as a function of the percentage of MMA in the initial MMA-PVC mixture for different VBTD contents on PVC, while Fig. 6 presents the variation of the ratio grafted PMMA/charged MMA as a function of the VBTD content in PVC. These plots can be explained as stated earlier: grafting of PMMA on modified PVC can occur according to two routes.

First, the classical grafting by chain transfer of a PMMA radical to the PVC backbone. The more labile the chlorine atom, the more this reaction predominates. Below 0.3-0.4% of VBTD in the PVC,

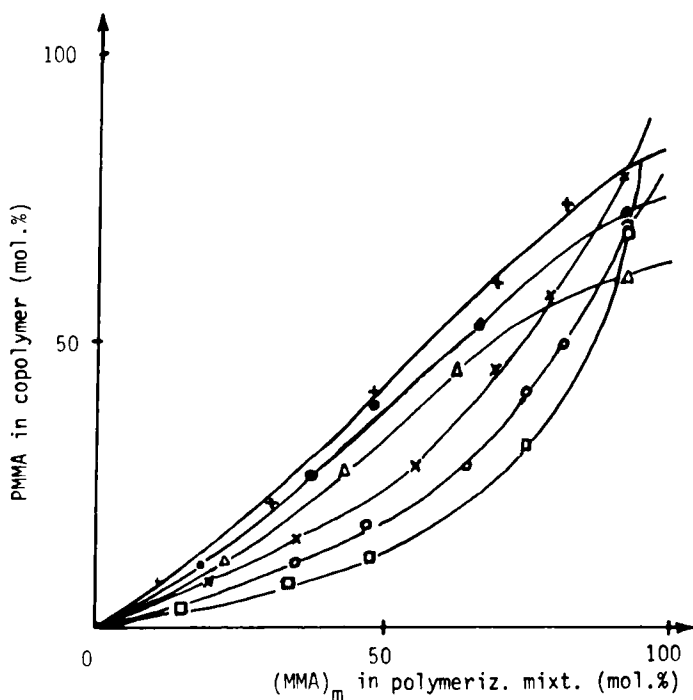


FIG. 5. Percentage of PMMA in PVC-g-PMMA as a function of the percentage of MMA in the polymerizable initial mixture and of the VBDT content in PVC (mol%): (\square), (VBDT) = 0.82; (\circ), (VBDT) = 0.65; (\times), (VBDT) = 0.50; (+), (VBDT) = 0.42; (\bullet), (VBDT) = 0.24; (\triangle), (VBDT) = 0.14.

there are many reactive chlorines (allylic or tertiary) which allow chain transfer just as does unmodified PVC (see Fig. 6 for VBDT = 0). However, AIBN is not very efficient as a free-radical initiator for this kind of reaction, and the grafting efficiency is low (0.32 for 66% MMA conversion). When the labile chlorine atoms are substituted by unreactive benzodithioate groups, grafting decreases sharply until it becomes negligible (Fig. 6, plot for benzodithioate-substituted PVC).

The second route is the copolymerization of MMA with the pendent styryl groups of PVC. This reaction is more rapid than the chain transfer, as demonstrated by the rapid increase of the grafting with VBDT content. Below 0.3-0.4%, both reactions, transfer and copolymerization, occur. The VBDT content in PVC remains low, and the probability of crosslinking by reacting VBDT groups on different PVC chains is very close to zero. For higher VBDT contents this possibility

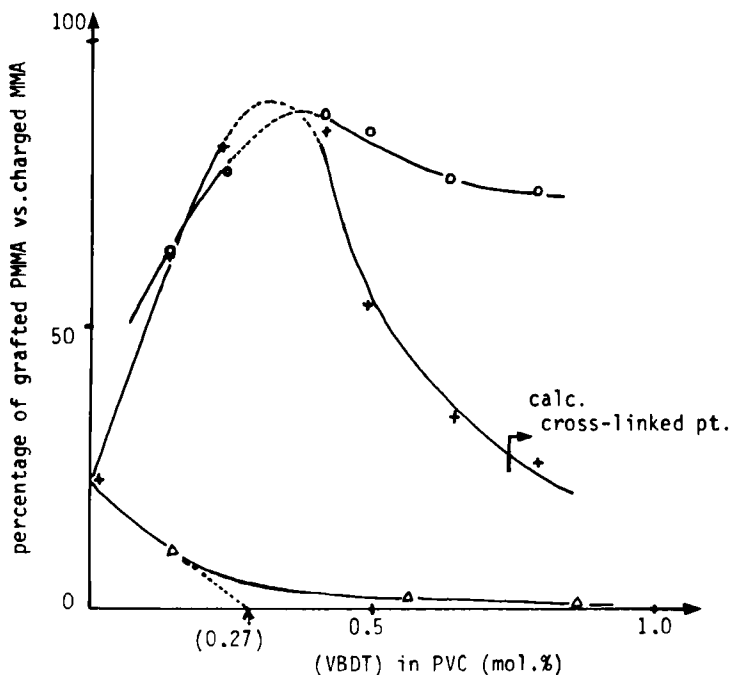


FIG. 6. Dependence of grafted PMMA as a percentage of charged MMA on the VBDT content of PVC. (○) Initial percentage of MMA in the polymerization mixture, $(\text{MMA})_m = 93\%$; calculated gel point according to Eq. (1): $(\text{VBDT}) = 2.37$ (mol%). (+) $(\text{MMA})_m = 48\%$; calculated gel point: $(\text{VBDT}) = 0.79\%$. (△) Grafting on benzodithio-substituted PVC.

exists, leading to crosslinking, thus lessening both the reactive sites for copolymerization and the diffusion rates of the reactants (monomer and, especially, polymeric radical) toward the remaining active sites. Thus, crosslinking appears to be the main cause of the limitation of grafting. The investigation of the crosslinking conditions showed that the influence of the concentration of AIBN and monomers were negligible, but that this phenomenon was highly dependent on the VBDT content and the MMA:VBDT ratio.

Figure 7 presents the conditions for the occurrence of crosslinking as a function of these parameters, which we have fitted to the following empirical equation (correlation coefficient: 0.986):

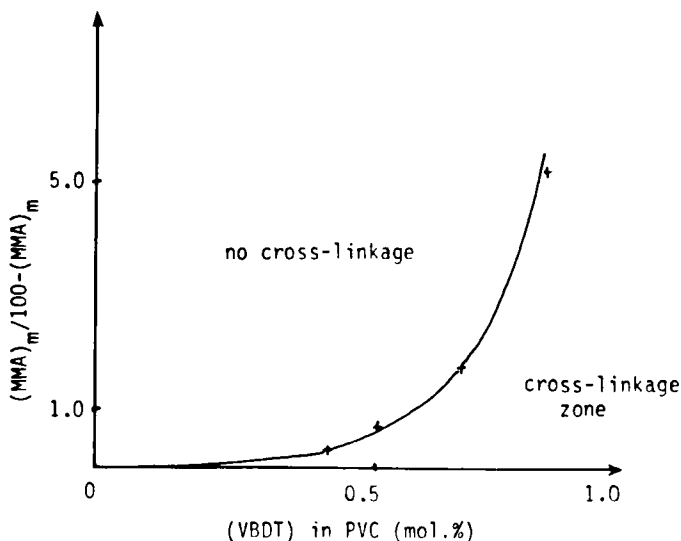


FIG. 7. Occurrence of crosslinking as a function of $(\text{MMA})_m$ and (VBDT) .

$$\frac{[\text{MMA}]_m}{100 - [\text{MMA}]_m} = 1.91 \times [\text{VBDT}]^{3.0}, \quad (1)$$

where $[\text{MMA}]_m$ is in mol% MMA in the monomer mixture and $[\text{VBDT}]$ is in mol% VBDT groups in PVC. This means that crosslinking will occur if the composition of the starting grafting mixture is such that

$$\log \frac{[\text{MMA}]_m}{1 - [\text{MMA}]_m} < 0.28 + 3.0 \log [\text{VBDT}].$$

Crosslinking for relatively low VBDT contents is consistent with the previously determined values of the reactivity ratios for the copolymerization of MMA with methyl p-vinylbenzodithioate (0.14 and 0.18) [22] although a strict extrapolation cannot be made from a simple monomeric compound to a particular vinyl structure such as 2.

The very high grafting efficiencies obtained in this way (Table 2)

are unusual compared to conventional free-radical grafting involving MMA and PVC [10]. This result can be attributed to the replacement of the most labile chlorine atoms which can be considered responsible for the retardant effect of reactive groups on the free-radical copolymerization of MMA [14]. The lower grafting efficiency observed for crosslinked copolymers is consistent with this hypothesis.

Microstructure Analysis

Generally, the random grafting and the unreactive character of the bonds between branches and backbone make it very difficult to determine the microstructure of a grafted copolymer, i.e., the average number of grafted chains per main chain macromolecule and the length of the branches. Nevertheless, this analysis becomes possible if the side-chains can be removed and separated easily from the backbone polymer [24].

Dithioesters react quickly at room temperature with a primary or secondary amine. This reaction is quantitative and yields a thiol and a thioamide without by-product [25]. It has been used for the synthesis of a large number of polythioamides from difunctional compounds [26] and for the attachment of various amino compounds (amino acids, peptides, dyestuffs) to dithioester-bearing polymers [27].

The reaction of piperidine with dissolved or swollen PVC-g-PMMA in THF leads to the removal of the PMMA branches grafted through benzodithioate groups (Fig. 8). Piperidine does not dehydrochlorinate PVC at room temperature. PMMA fraction 9 was extracted by hot benzene, while thiol-bearing PVC 10 crosslinked quickly, yielding 11. The molecular weights and the \overline{DP}_n of the PMMA sidechains were determined by GPC and by UV analysis by comparing the UV absorption of the thioamide groups on PMMA 9 (previously determined on a model, p-isopropylbenzothiopiperamide 12, $\lambda_{\max} = 283.4 \text{ nm}$, $\log \epsilon = 4.11$) to that of the methacrylate ($\lambda_{\max} = 226 \text{ nm}$, $\log \epsilon = 2.17$, solvent acetonitrile). Postulating one or two thioamide groups per PMMA chain gave satisfactory agreement between the two methods (see Table 3).

Analysis of the PVC fraction showed that some PMMA chains remain grafted on the PVC and that no further treatment by piperidine can remove them, even at 60°C. This is attributed to PMMA grafted by chain transfer (4), and its percentage was determined by elemental analysis (% C, % Cl) and IR spectroscopy (Fig. 9). The relative importance of chain-transfer-grafted PMMA decreases when the number of polymerizable sites increases to the gel point, beyond which it begins to grow slowly due to the consumption of copolymerizable styryl groups by crosslinking. However, given the low reactivity of the secondary chlorine and the limited accessibility of the few residual reactive chlorine due to the gel effect, this growth is very slow. The

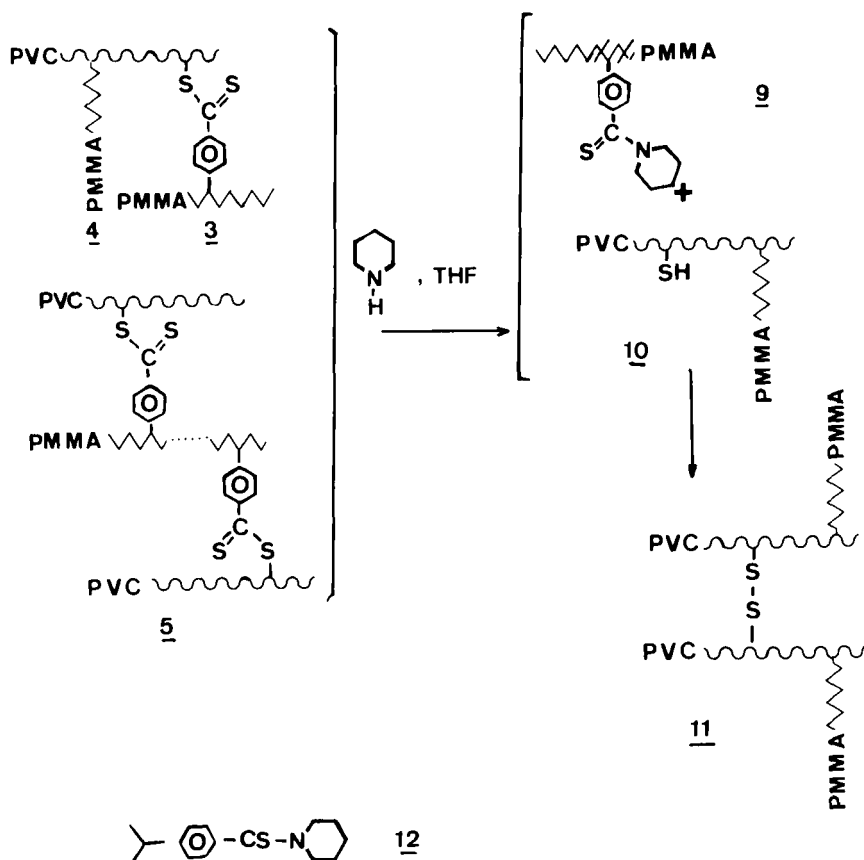


FIG. 8. Removal of PMMA sidechains by piperidine.

randomness number and length of these sidechains are not easily measurable, but below 0.5% VBTD there are few such sidechains, and a good description of the overall structure of PVC-g-PMMA can be obtained.

Postulating that each VBTD group bears a PMMA chain and no degradation of the PVC backbone occurs during grafting makes it possible to calculate M_n of the soluble PVC-g-PMMA since the average number of VBTD groups per macromolecule of PVC is known. The calculated values are consistent with the experimental data determined by GPC, taking into consideration that branched polymers behave like lower molecular weight species in GPC [28].

TABLE 3. Microstructure Analysis of PVC-g-PMMA

Overall characteristics of PVC-g-PMMA			Removed PMMA sidechains			Detailed composition of PVC-g-PMMA			
% PMMA (UV or IR), mol %	Average number of Moiety 2 per macromolecule, mol %	\bar{M}_n (GPC)	\bar{M}_w (GPC)	\bar{M}_n (GPC)	\bar{M}_w (GPC)	\bar{M}_n (UV)	% g-PMMA by chain transfer vs total PMMA ^a	\bar{M}_n (calculated) ^b	\bar{M}_n (calc)
28	2.0	32 500	64 200	6 000	11 700	6 200 ^c	12	39 660	0.82
49	2.4	44 000	93 400	11 000	28 300	14 500 ^c	7	55 740	0.77
18 ^e	2.4	-	-	3 000	6 780	2 800 ^d	14	-	-
12 ^e	3.2	-	-	1 500	3 200	1 450 ^d	16	-	-
68	3.2	40 300	104 500	8 700	20 100	8 400 ^c	6	54 000	0.75

^aEstimated value according to the plots of Fig. 9 and elemental analysis of Fractions 11.

^bCalculated \bar{M}_n of removed PMMA sidechains by the average value of UV and GPC determinations, including the estimated value of g-PMMA by chain transfer, postulating no degradation of the PVC backbone.

^cOne thioamide group per PMMA chain.

^dTwo thioamide groups per PMMA chain.

^eCrosslinked copolymer.

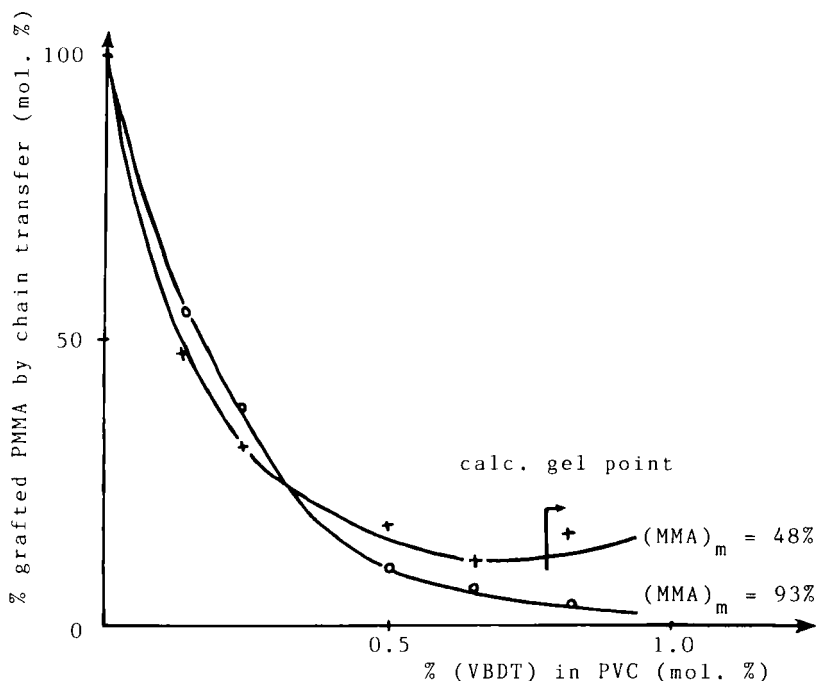


FIG. 9. Variation of the percentage of PMMA grafted by chain transfer with (VBDT) in PVC. (+): $(MMA)_m = 48\%$, calculated gel point; (VBDT) = 0.79%. (o): $(MMA)_m = 93\%$, calculated gel point; (VBDT) = 2.37%.

PHYSICOCHEMICAL ANALYSIS

Viscosity

Evidence of grafting is provided by the dependence of the inherent viscosity (which approximates the intrinsic viscosity $[\eta]$ for low polymer concentrations) of THF solutions of grafted PVC on the temperature and the PMMA content (Fig. 10).

The decrease of the viscosity for high PMMA content may be explained by branching [29] together with distortion of the conformation of the two incompatible polymer chains [30], while the temperature dependence is regarded as indicating a grafted copolymer [8b, 31] although no satisfactory explanation has yet been advanced to explain these data.

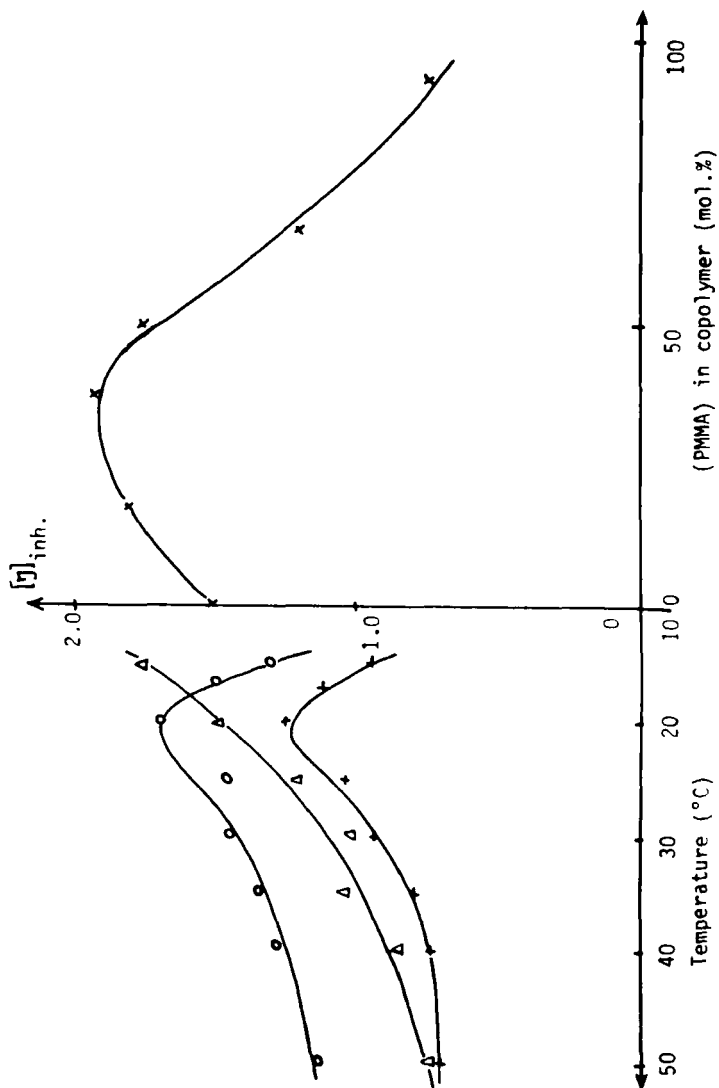


FIG. 10. Variation of the inherent viscosity of PVC-g-PMMA bearing two PMMA branches per macromolecule vs PMMA content (right) and temperature (left). (○) 55% PMMA (mol%) in PVC-g-PMMA, (+) 79% PMMA in PVC-g-PMMA, (Δ) ungrafted 0.5% VBDT-containing PVC.

Glass Transition Temperature

This analysis was carried out with a 41% PMMA PVC-g-PMMA (Fig. 11) under nitrogen. Only one T_g is evident on the thermogram, indicating only one phase in the grafted copolymer. The beginning of the transition occurs at 359 K (86 °C), which is approximately the T_g of PVC (354 K). A marked transition is exhibited at 369 K (96 °C), while the end of the transition is estimated at around 384 K (112 °C). The observed T_g for the PVC-g-PMMA is 369 K, between the T_g 's of the two constituents (PVC = 354 K, PMMA = 378 K [32]). It is consistent with the value calculated (370 K) according to the empirical theory of the additive properties of the glass transition function developed by Van Krevelen and Hoftyzer [33].

The thermogram shows significant differences from that of a blend of PVC and PMMA (Fig. 11). This indicates that the two polymers are highly aggregated in the graft, as confirmed by the transparency (or the very slight turbidity) of films of PVC-g-PMMA obtained by evaporation of their THF solution on a glass plate, while the complete opacity of films of blends is proof of the incompatibility of the two components.

Thermal Stability (Fig. 12)

PVC is very heat sensitive, and the degradation occurs in two steps: dehydrochloration followed by chain scission. Interactions between PVC and various compounds blended into it can improve or reduce the thermal stability [34]. For blends of polymers, the compatibility between the components has been found to be one of the most important factors governing the heat sensitivity. In particular, small amounts of PMMA (1-10%) blended into PVC lead to a drop of the dehydrochloration temperature of about 5 to 15 °C [35]. Our study has been limited to the dehydrochloration phase of PVC. All runs were conducted under nitrogen flow. Samples of pure PVC, 0.24% VBDT-containing PVC, and PVC-g-PMMA (41% PMMA) were heated at 180 °C for 2.5 h. Degradation occurred at 0.1, 2.1, and 2.2 h, respectively. Substitution of labile chlorines by dithioester groups delays the dehydrochloration. Grafting of PMMA to PVC, yielding a one-phase copolymer, enhances the heat stability [31] in contrast to the reported behavior of a blend [35].

CONCLUSION

Our work has resulted in PVC highly grafted with PMMA with use of AIBN as free-radical initiator. In contrast to many types of conventional grafting by chain transfer, our results allow the prediction of the final PVC-g-PMMA with fair reliability. The presence of benzodithio-

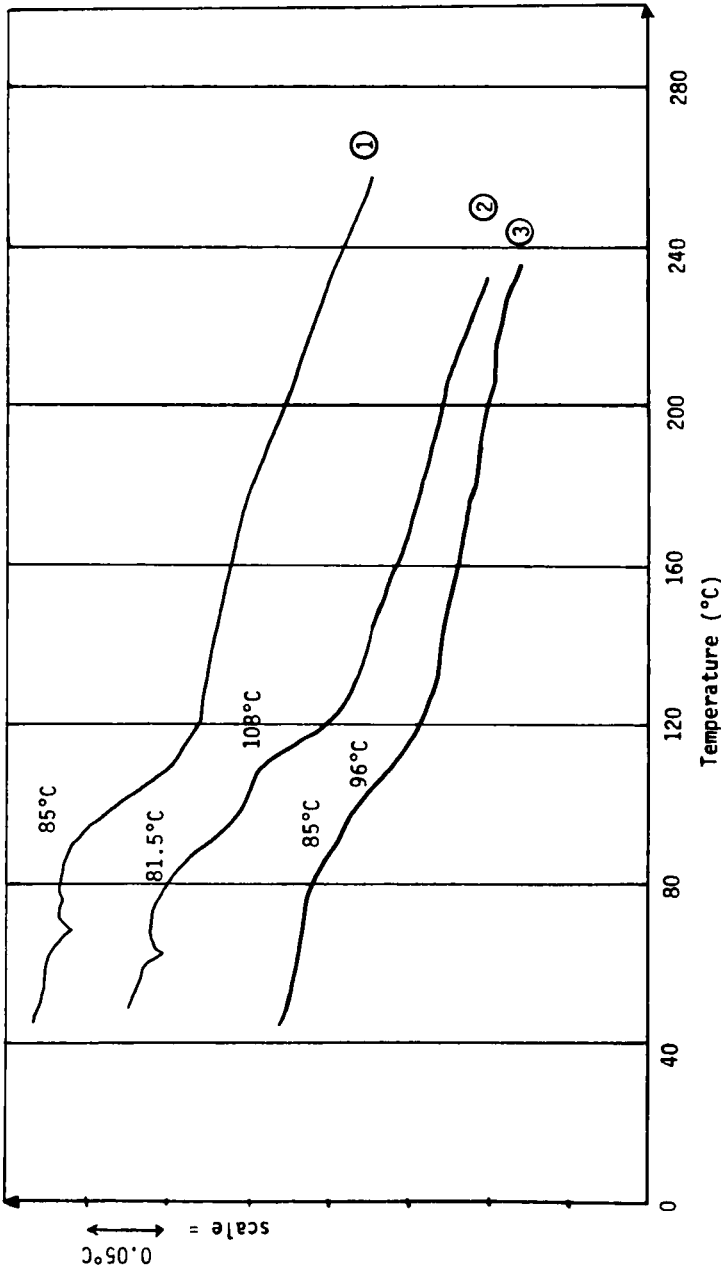


FIG. 11. Thermograms of ① 0.50% VBDT-containing PVC, ② 60-40 PVC-PMMA blend, ③ PVC-g-PMMA (41% PMMA). Heating rate = 20°C/min, sample weight = 2.0 mg in sealed dish.

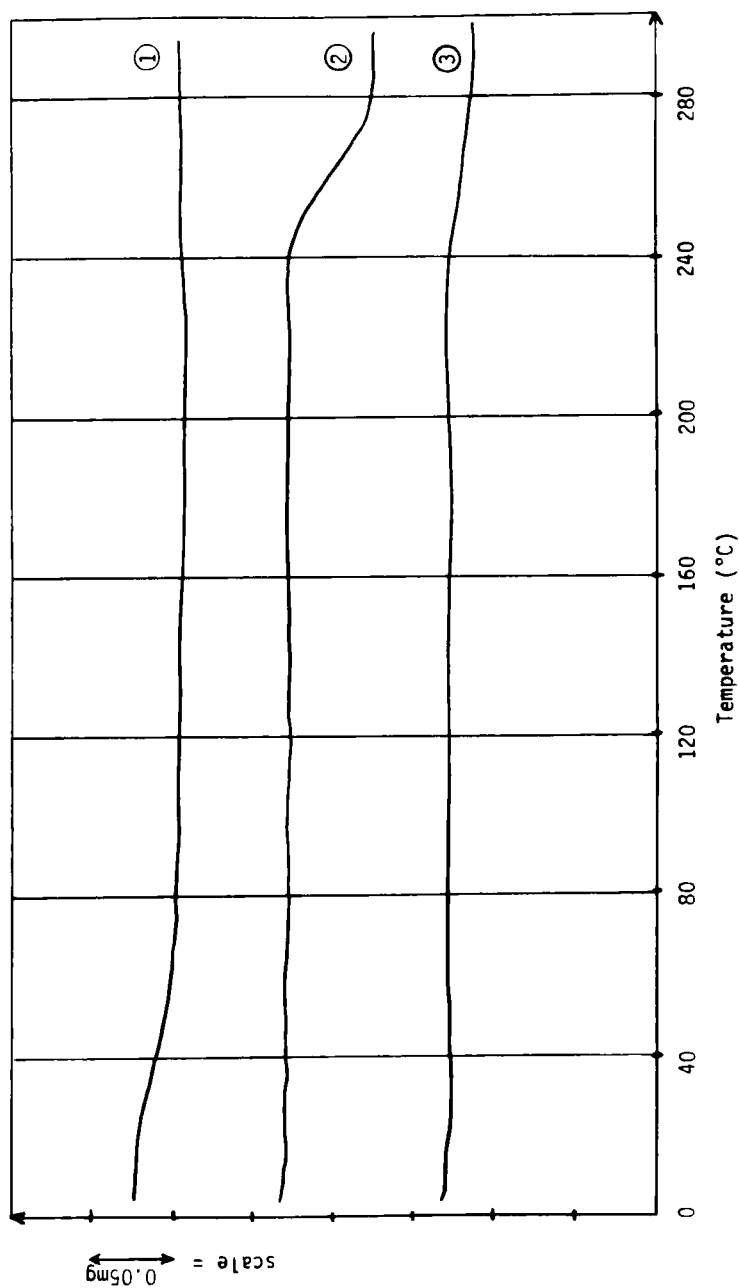


FIG. 12. Thermal stability of ① pure PVC, ② 0.24% VBDT-containing PVC, ③ PVC-g-PMMA (41% PMMA). Heating rate = 20°C/min, sample weight = 5.5 mg in sealed dish.

ate groups between PVC and the PMMA sidechains allows the removal of the latter and, therefore, reliable determination of the structure of the copolymer. Moreover, it can improve the UV stability of the polymer. Thermal stability and glass transition temperature are consistent with the one-phase character of the graft copolymer.

The high reactivity of vinyl benzodithioate salts toward halogen atoms allows the extension of this grafting method to other types of halogenated trunk polymers and other monomers. For example, positive results were recently obtained by the free-radical copolymerization of chlorinated polydimethylsiloxane [36] bearing VBDT groups and styrene. Further developments of this technique are under investigation.

Additional details about calculations and experimental details can be supplied on request.

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