

Synthesis of Acetoxy-*n*-chloroparaffins and Their Evaluation as Plasticizers for PVC

INTRODUCTION

Chlorinated paraffins have been used as additives for PVC mainly to reduce the cost in formulations and to increase the fire retardancy of articles containing chiefly phthalate plasticizers. The lack of compatibility of these materials with PVC makes them unsuitable as primary plasticizers. Rosenberg¹ has determined that both the chlorine content and the average chain length of the materials play an important part in defining the plasticizing properties of these materials. Thus, he found that the efficiency of chloroparaffinic plasticizers increased as the chlorine content, chain length, and viscosity were reduced. Reducing chain length at constant chlorine content reduces the viscosity and increases the penetrating power of the plasticizer. Increasing the amount of chlorine 35%–55% reduces the plasticizer efficiency.

The efficiency of a plasticizer depends on several factors, of which Mark and Immergut² have listed size of the molecule, compatibility between polymer and plasticizer, and diffusion rate as most important. In this study attempts have been made to increase the compatibility of PVC–chloroparaffin mixtures by increasing the polarity of the chloroparaffins. It was hoped that the plasticizer efficiency would also increase. Thus, a paraffinic fraction having an average carbon-number of 26 was chlorinated thermally to 38% Cl by weight. Approximately 6% of the chlorine atoms were substituted by acetoxy groups. Acetoxy groups were chosen since the most common plasticizers for PVC are esters and because it was felt that the reaction for the preparation of acetoxy-*n*-chloroparaffins would be straightforward.

EXPERIMENTAL

Chloroparaffins were prepared as described previously.³ Characterization of the paraffins used as starting materials has also been described.⁴ Acetoxy-*n*-chloroparaffins were prepared by reacting *n*-chloroparaffins (38 wt-% Cl) with potassium acetate in an excess of acetic acid at reflux temperature following a well-known reaction procedure.⁵ The amount of chlorine was determined by the well-known Schonigers method and is considered reliable to ± 2 wt-% Cl. Since both elimination and substitution reactions can occur, infrared spectroscopy was used to follow elimination (trans disubstituted double bond, 970 cm^{-1}) and substitution (ester group, 1735 cm^{-1}). Several solvent systems were utilized to optimize the yield of the desired product. It was found that in dimethyl sulfoxide, elimination of HCl predominated at the reflux temperature of the mixture.

The following procedure was used to synthesize 1.5 kg acetoxy-*n*-chloroparaffins (32% Cl by wt). To 0.25 mole chloroparaffin (ave. mol. wt 450) were added 0.5 mole potassium acetate and 2.5 moles glacial acetic acid. The mixture was well stirred for 24 hr at the reflux temperature of acetic acid. After cooling, the mixture was extracted with ether. The ether layer was washed with water repeatedly until the wash water was neutral. After the ether was evaporated, a yellowish viscous

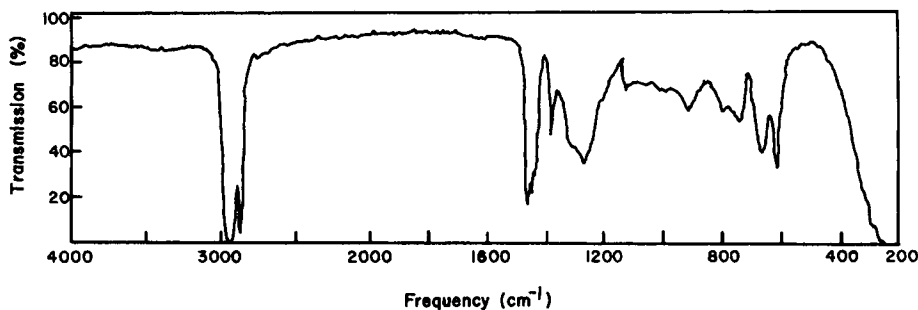


Fig. 1. IR spectrum of chloroparaffin.

material was obtained. It was found that longer reaction times yielded more elimination product as evidence by darkening of the product. Six wt-% Cl was considered substituted by acetoxy groups as shown by infrared analysis. Attempts to determine saponification equivalents were not successful because chloride interfered.⁶

Infrared spectra of all the samples were determined on a PE Model 577 spectrometer from liquid films on NaBr plates. Thermogravimetric analysis (TGA) of the samples was carried out using a du Pont 951 thermobalance coupled to a 990 console at a heating rate of 20°C/min under a N₂ atmosphere.

The modulus at 100% elongation for mixtures of PVC–dioctyl phthalate (DOP), PVC–chloroparaffin (CP), PVC–acetoxy-*n*-chloroparaffin (ACP), PVC–DOP–CP, and PVC–DOP–ACP were determined. Standard ASTM procedures were followed to prepare test samples (ASTM D647-88) in a Guiz Model 1205S roll mill and to determine moduli (ASTM D648-68) on an Instron Model 1113 tester. A Haake Rheochord E equipped with a cam mixer was used to determine melt characteristics of the blends. A standard recipe was used that consisted of 100 parts PVC, 2.00 parts of a commercial organo-lead stabilizer, 0.5 part stearic acid, and variable amounts of plasticizer.

RESULTS AND DISCUSSION

Synthesis of Acetoxy-*n*-chloroparaffin

Figures 1 and 2 show IR spectra of the starting material and of the product. Figure 3 shows the spectrum of a product considered to be a combination substitution–elimination product. While substitution reactions with lower molecular weight alkyl chlorides are straightforward, the same is not true of the paraffinic secondary chlorides. At first it was considered that the poor solubility of the starting material was responsible for the low substitution. However, Lanchec has shown⁷ that it is easier to convert paraffinic chlorides to olefins than to alcohols or ethers by substitution under most conditions. We found that by increasing the solubility of the starting material in DMSO, higher yields of olefins were obtained. From Figure 3 it can be seen that the C–Cl bonds (600–700 cm⁻¹) have almost disappeared, but the ester bonds do not increase as expected if all Cl groups are replaced by acetate. In fact, a black tar is obtained as product.

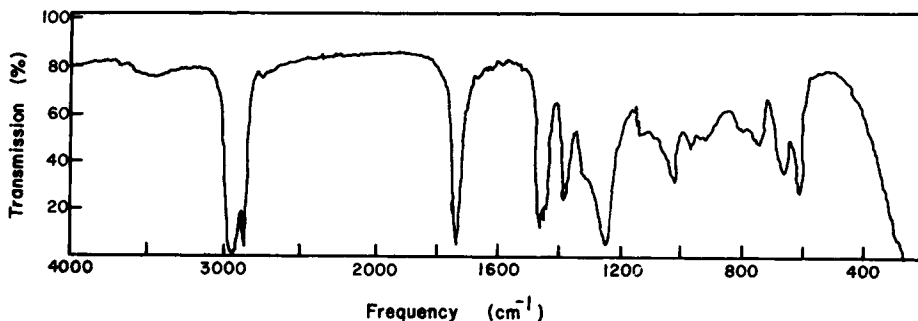


Fig. 2. IR spectrum of acetoxy-*n*-chloroparaffin.

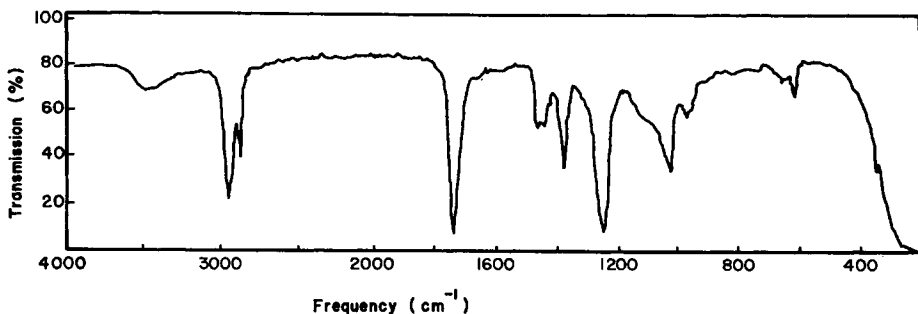


Fig. 3. IR spectrum of degraded acetoxy-*n*-chloroparaffin.

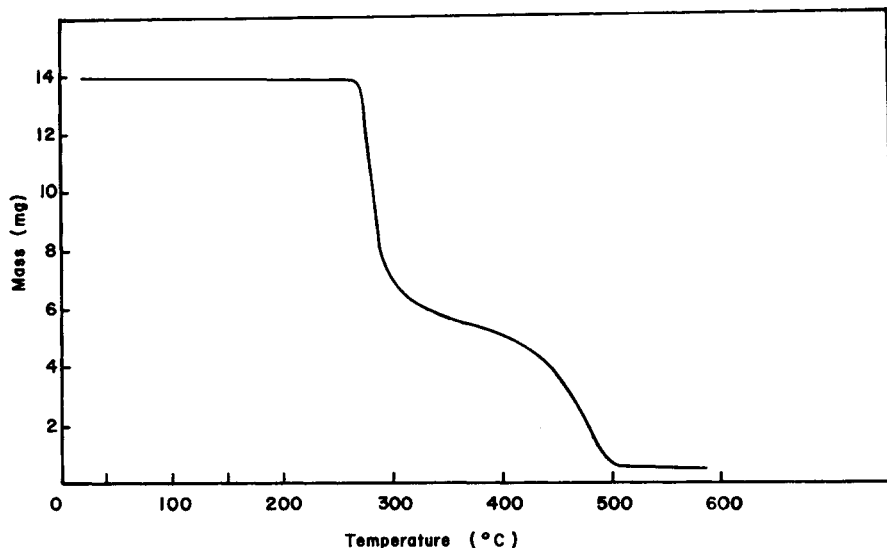


Fig. 4. TGA trace of chloroparaffin (38 wt-% Cl).

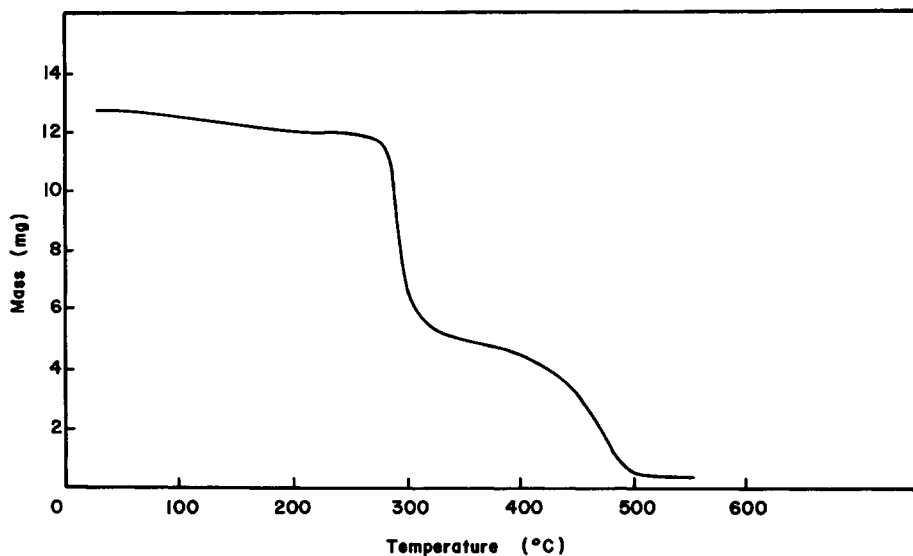


Fig. 5. TGA trace of acetoxy-*n*-chloroparaffin.

Figures 4 and 5 show the thermal gravimetric curves for both the starting material and the product, respectively. Since the amount of chlorine substituted was around 6%, the thermal behavior of both materials was expected to be similar. On the other hand, the starting material turned black after 10 min at 175°C in air, while the acetoxy-*n*-chloroparaffins turned black after 30 min. The product was more stable toward discoloration. This may be because the more labile chlorine atoms were probably the only ones substituted by acetate groups. Recently, crown ethers have been used to promote the substitution of chlorine groups by acetate groups,⁸ so that a better route to the modification of chloroparaffins may be available.

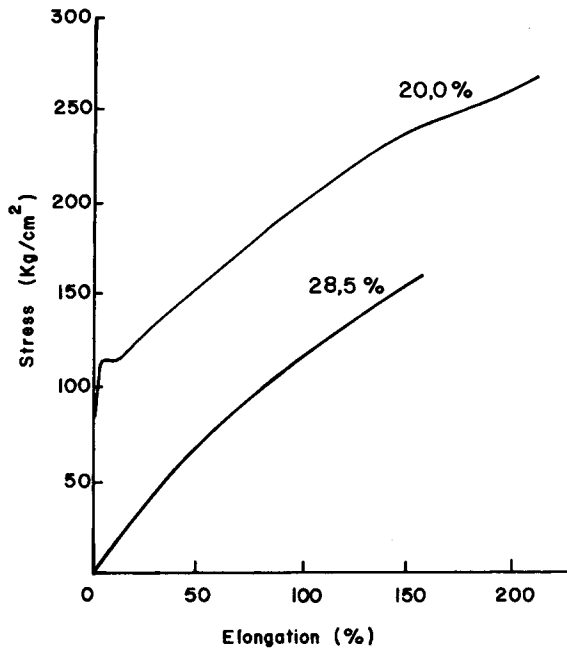


Fig. 6. Stress-strain curve for PVC plasticized with diethyl phthalate (DOP).

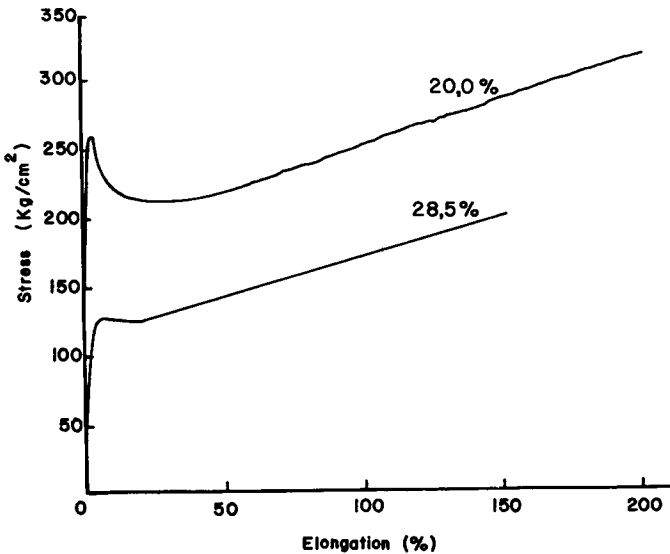


Fig. 7. Stress-strain curve for PVC plasticized with acetoxy-*n*-chloroparaffin (ACP).

Evaluation of Acetoxy-*n*-chloroparaffins (ACP) as Plasticizers for PVC

The plasticizer efficiency for ACP was obtained by comparison to DOP and to the CP. Throughout this discussion the ACP that was synthesized is considered to have around 32 wt-% Cl. The remaining 6 wt-% Cl was substituted by acetate groups.

Figures 6-8 show stress-strain curves for DOP, CP, and ACP at 20.0 and 28.5 wt-% loadings of plasticizer to PVC resin. The curve at 28.5% loading of DOP shows a behavior typical of soft and tough materials, while all the other curves show typical hard and tough behavior. Higher loadings of CP and ACP were not possible due to the incompatibility of the materials as shown by a "loop

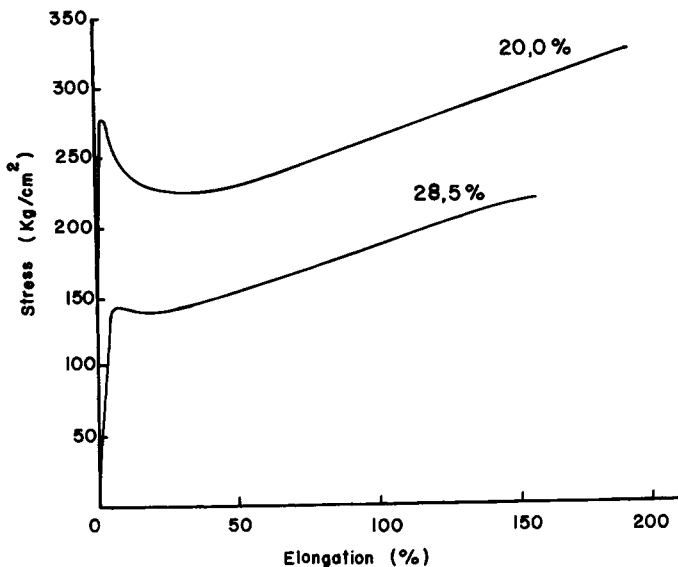


Fig. 8. Stress-strain curve for PVC plasticized with chloroparaffin (CP).

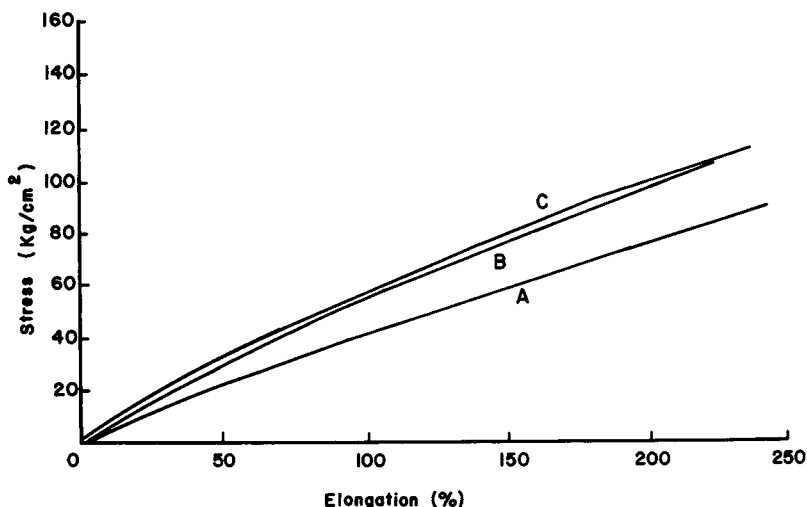


Fig. 9. Stress-strain curve for PVC plasticized with: (A) 40 wt-% DOP; (B) 30 wt-% DOP + 10 wt-% ACP; (C) 30 wt-% DOP + 10 wt-% CP.

test." Lower loadings of all three materials yielded very poor test samples. Table I summarizes the data obtained from tensile tests.

These results show that ACP at both loadings has a somewhat lower modulus than CP, so that its plasticizer efficiency is higher than that of CP but not as high as that of DOP. At a 28.5% loading, ACP increases the modulus 58% and CP increases it 66% over DOP.

Figure 9 shows stress-strain curves for plasticized PVC with 40 wt-% DOP, 30 wt-% DOP + 10 wt-% ACP, and 30 wt-% DOP + 10 wt-% CP. Replacing part of the DOP by ACP or CP increases the toughness of the materials; however, there is a very slight difference between ACP and CP. Chloroparaffins have been used in many formulations in this manner.⁹ Apparently, the use of ACP offers no advantage when mixed with DOP.

Figures 10-12 show rheograms for mixtures containing 28.5 wt-% of DOP, ACP, and CP, respectively. In Figure 9 it can be seen that the fusion peak *b* occurs immediately after the loading peak *a*. This occurs because DOP is incorporated in the resin immediately. A constant mixing torque

TABLE I
Modulus at 100% Elongation for PVC with Different Plasticizers

Plasticizer	Plasticizer loading, wt-%	Modulus (deviation), ^a kg/cm ²
DOP	20.0	200 ± 5
	28.5	107 ± 5
ACP	20.0	245 ± 7
	28.5	169 ± 4
CP	20.0	256 ± 7
	28.5	178 ± 5

^a Deviation for six samples.

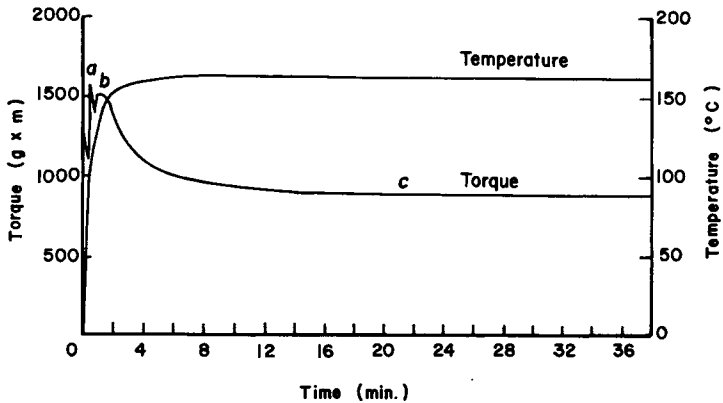


Fig. 10. Torque and temperature vs time for PVC with 28.5 wt-% DOP.

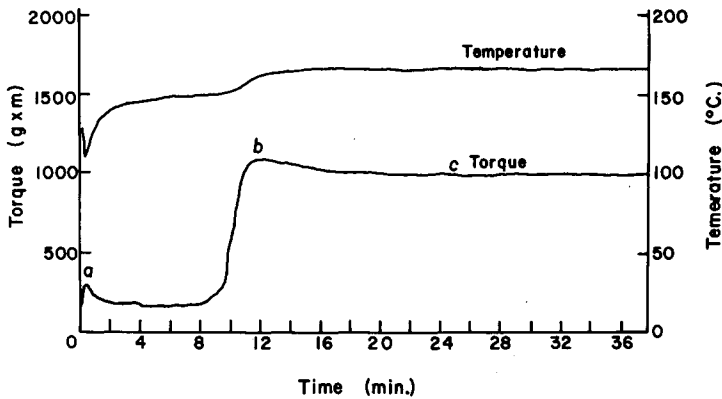


Fig. 11. Torque and temperature vs time for PVC plasticized with 28.5 wt-% ACP.

is reached after 5 min of mixing. Figures 10 and 11 show that both ACP and CP influence the magnitude of the loading peak and very significantly the time necessary for fusion. Table II summarizes the results of these tests.

The trend shown by the data is that higher torque values are associated with the better plasticizer and shorter times are required for fusion. Thus, some improvement in the plasticizing ability of ACP is noticed. Point D in Figure 12 shows that degradation leading to crosslinking occurs after 34 min of mixing at 168°C.

Finally, Figure 13 shows a rheogram of a sample containing 30 wt-% DOP + 10 wt-% ACP. As DOP is replaced, the time required for fusion is slightly increased and the torque at the fusion peak is decreased.

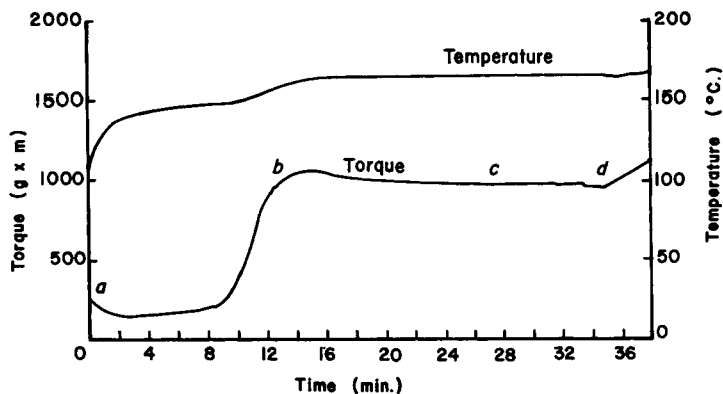


Fig. 12. Torque and temperature for PVC plasticized with 28.5 wt-% CP.

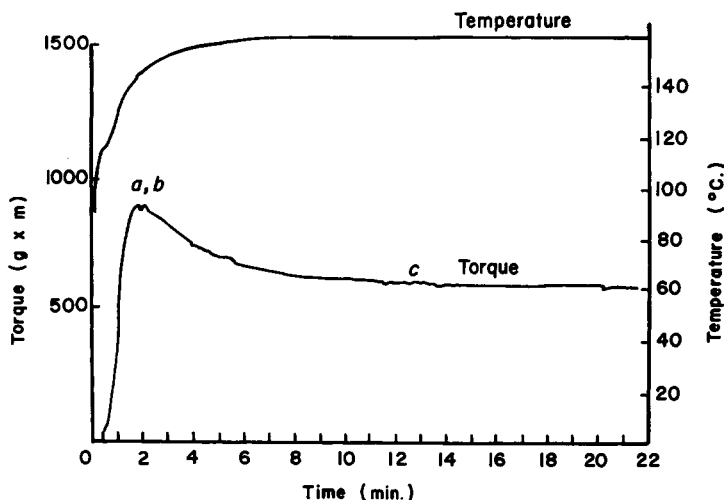


Fig. 13. Torque and temperature vs time for PVC plasticized with 30 wt-% DOP and 10 wt-% ACP.

TABLE II
Torque and Time Associated with Fusion Peaks for Plasticized PVC

Plasticizer ^a	Torque, m g	Time, ^b sec
DOP	1530 ± 50	72 ± 4
ACP	1130 ± 15	666 ± 60
CP	1080 ± 25	750 ± 60

^a Loading of 28.5 wt-%.

^b The experimental procedure utilized to load the sample in the Rheomix 600 is in part responsible for the wide deviation. Samples were preblended in a beaker, weighed, and then placed in the loading chute. Values shown are an average for five runs.

Both stress-strain and rheological measurements indicate that the efficiency of *n*-chloroparaffins as plasticizers can be improved slightly by the incorporation of acetate groups. It is of interest to see if more substitution of Cl by acetate will yield better plasticizers. Also the influence of other groups needs to be studied. While both of these ideas were considered, a better synthetic route needs to be worked out before the synthesis of other compounds are attempted.

CONCLUSIONS

A chloroparaffin (average mol. wt 450, 38 wt-% Cl) was treated with potassium acetate in acetic acid to produce an acetoxy chloroparaffin. The product was characterized by infrared spectroscopy and is considered to contain 32 wt-% Cl and 6 wt-% Cl replaced by acetate groups. TGA shows that the material behaves similar to the starting material. The product is more stable toward discoloration at 175°C in air than the starting material. This is believed to be due to the substitution of the more labile chlorine atoms. The synthetic route yields both elimination and substitution products so that it is not considered suitable for higher substituted products.

The plasticizer efficiency of the product increases slightly over the chlorinated paraffin. Both chloroparaffin and acetoxy-*n*-chloroparaffin were compared to dioctyl phthalate by determining the modulus at 100% elongation and by obtaining the melt behavior in a Haake torquemeter. Tests show that the plasticizer efficiency is increased by making the chloroparaffins more polar by adding acetate groups.

References

1. D. H. Rosenberg, *Adv. Chem. Ser.*, **48**, 108 (1965).
2. E. H. Immergut and H. F. Mark, *Adv. Chem. Ser.*, **48**, 1 (1965).
3. J. M. Sosa, *Br. Polym. J.*, **7**, 161 (1975).
4. J. M. Sosa, *J. Polym. Sci.*, **13**, 2397 (1975).
5. L. Gatterman, *The Practical Methods of Organic Chemistry*, Macmillan, New York, 1918, p. 197.
6. R. L. Shriner, R. C. Fison, and D. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., Wiley, New York, 1956, p. 235.
7. G. Lanchec, *Chim. Ind.*, **93**, 662 (1965).
8. J. E. L. Roovers and S. Bywater, *Macromolecules*, **9**, 875 (1976).
9. *Evaluation of Chlorinated Paraffins as Secondary Plasticizers for Polyvinyl Chloride*, EC-CW-5, Diamond Shamrock Corp., 1970.

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