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Telomeric Plasticizers: Cotelomers Based on Vinylchloride and Carbontetrachloride

HADASSA ROSIN, S. L. J. DAREN, M. ASSCHER, and D. VOFSI,
Department of Plastics Research, The Weizmann Institute of Science, Rehovot, Israel

Synopsis

Cotelomers of vinylchloride and other monomers (acrylate esters, diethyl maleate, diethyl fumarate, ethylene, propylene, and butene-1) have been prepared in order to evaluate their properties as plasticizers for poly(vinyl chloride). With the electron-acceptor ester-monomers, cotelomers with carbon tetrachloride of an average molecular weight of 500–900 were obtained, using iron chloride as the catalyst. Ethylene, propylene, and butene-1 gave lower molecular weights and a considerable amount of distillable telomers. Ethylene, vinyl chloride, and carbon tetrachloride gave cotelomers with a molecular weight in the range 400–750, when the telomerization was initiated by ethanolamine or by azobisisobutyronitrile. These initiation systems gave a much reduced volatile fraction.

INTRODUCTION

Whenever a vinylic monomer is polymerized in the presence of carbon tetrachloride and of a source of free radicals, a polymer of a low molecular weight is obtained, owing to chain transfer.[1] The reduction in molecular weight depends on the nature of the monomer; but, with the exception of vinyl esters or ethers, 1:1 adducts are never formed in more than a very small proportion.[2]

Chain transfer by carbon tetrachloride is very strongly catalyzed by copper chloride (redox transfer), and then the 1:1 adduct is the sole product.[3] With catalysis by iron chloride, the situation is in between, and telomers are obtained together with varying amounts of 1:1 adducts.[3] Thus, a range of molecular weights becomes accessible which would be difficult to attain in other ways.

Zilberman et al.[4] have applied iron chloride catalysis to the telomerization of vinyl chloride and carbon tetrachloride. The telomers $CCl_3(CH_2-CHCl)_nCl$ with $\bar{n} = 1–3$ were mobile liquids, those with $\bar{n} > 7$ were very viscous, and those with $\bar{n} > 8$ were solids. Saveliev and his coworkers[5] found that these telomers were PVC plasticizers with an excellent compatibility, resulting in a low migration and a high resistance to solvent extraction, even with as much as 100 pph plasticizer. On the other hand, the low-temperature performance appeared to be poor, and so did the efficiency, as was apparent from the small change in glass transition temperature (T_g) with increasing amount of plasticizer.

One objective of the present work was to improve the performance of the telomeric plasticizers based on vinyl chloride, and another, to extend their useful liquid range.

Out attempt to achieve this has been based on a study of the cotelomerization of vinyl chloride with other vinylic monomers and olefins.

CHOICE OF COMONOMER

The chain mechanism for the iron chloride-catalyzed telomerization is as follows[3,6]:

Initiation:

$$\mathrm{Fe^{3+}} + \text{reducing agent} \rightarrow \mathrm{Fe^{2+}} + \text{product} \tag{1}$$

$$\mathrm{Fe^{2+}} + \mathrm{CCl_4} \rightleftarrows \mathrm{FeCl^{2+}} + \cdot\mathrm{CCl_3} \tag{2}$$

$$\cdot\mathrm{CCl_3} + \mathrm{C{=}C} \rightarrow \mathrm{CCl_3{-}C{-}C}\cdot \tag{3}$$

Propagation:

$$\mathrm{CCl_3{-}C{-}C}\cdot + n(\mathrm{C{=}C}) \rightarrow \mathrm{CCl_3(C{-}C)}\cdot_{n+1} \tag{4}$$

$$\mathrm{CCl_3{-}C{-}C}\cdot + \mathrm{FeCl^{2+}} \rightarrow \mathrm{Fe^{2+}} + \mathrm{CCl_3{-}C{-}C{-}Cl}(1{:}1 \text{ adduct}) \tag{5}$$

$$\mathrm{CCl_3(C{-}C)}\cdot_{n+1} + \mathrm{FeCl^{2+}} \rightarrow \mathrm{Fe^{2+}} + \mathrm{CCl_3(C{-}C)_{n+1}Cl} \text{ (telomer)} \tag{6}$$

Termination:

$$\mathrm{Fe^{2+}} + \cdot\mathrm{CCl_3} \rightleftarrows \mathrm{Fe(CCl_3)^{2+}} \rightarrow \mathrm{FeCl^{2+}} + \text{products} \tag{7}$$

Vinylic monomers of the acceptor type,[7] e.g., acrylate esters or acrylonitrile, give in reaction (3) a radical which reacts slower with ferric chloride, step (5), than one derived from a donor-type monomer.[8] As a consequence, acceptor monomers give much higher telomers. Low telomers and 1:1 adduct are obtained from monomers with unreactive double bonds such as vinyl chloride, which give radicals, step (3), that are highly reactive in general and highly reactive toward ferric chloride in particular.

Unfortunately, the comonomer most commonly used with vinyl chloride, vinyl acetate, gave unstable and discolored cotelomers. Moreover, the radicals derived from vinyl acetate in step (3) are so reactive toward ferric chloride, step (5), that large amounts of 1:1 adduct were formed.

The copolymerization–reactivity ratios of vinyl chloride and acrylic esters or acrylonitrile are such[9] that even with a large excess of vinyl chloride in the feed, the growing chains will have predominantly acrylate ends. Owing to their slower reaction with ferric chloride,[8] step (6), telomers of a higher molecular weight are obtained (in the range 500–900) as compared to those derived from vinyl chloride alone.

Acrylonitrile–vinyl chloride cotelomers were badly discolored resins which did not appear to hold much promise.

Other acceptor monomers tried were diethyl maleate and diethyl fumarate. The reactivity ratios of the latter and vinyl chloride are more suitable for cotelomerization than those of the acrylic esters, and consequently a large excess of vinyl chloride in the feed is not needed. In our system, maleate probably reacts via prior isomerization to fumarate.

Reactive donor monomers like styrene and butadiene copolymerize very badly with vinyl chloride and were therefore not tried in the present work.

Finally, ethylene, propylene, and butene-1, although less reactive than vinyl chloride, are known to copolymerize with it rather well. We found accordingly that, at a manageable excess of these olefins over vinyl chloride, cotelomers containing olefin units could be produced. The molecular weights were rather low (360–440), and a large proportion of distillable products (1:1 adducts and low telomers) was obtained. With ethylene, a variant of the redox-transfer catalysis was used,[10] which enables the production of cotelomers with a higher molecular weight (400–900) at the expense of the low-boiling fractions.

All the obtained cotelomers were moderate- to high-viscosity liquids. The liquid range was extended well beyond that of the vinyl chloride–carbon tetrachloride homotelomers $CCl_3(CH_2CHCl)_nCl$, which are solid at room temperature for $n > 8$, i.e., MW of 650 and above.

CHOICE OF THE INITIATOR

In the present work, ferric chloride hexahydrate was used as the catalyst, in conjunction with a reducing agent which was to supply ferrous chloride throughout the reaction. The reduction may be effected by a source of free radicals that reduce ferric chloride,[11] e.g., azobisisobutyronitrile, or by other reducing agents. (For the initiation of a redox transfer chain, step (1), the formation of radicals is not essential.)

In his work on the homotelomerization of vinyl chloride and carbon tetrachloride, Zilberman et al.[4] used ferrous chloride as the catalyst. His reactions were carried out in a stainless steel autoclave.

Benzoin was a very convenient initiator[3,12] as far as reaction rates and conversions were concerned. Unfortunately, the produced cotelomers had a yellow color and were thermally unstable.

Powdered iron was reported to give satisfactory results, either alone or in conjunction with iron chloride, but was not used by us, since the level of dissolved iron increased during the reaction, and a correlation between the concentration of the catalyst and molecular weight of the product could not be made. For most of this work, we used isobutyraldehyde, which initiated the reaction in a homogeneous system, slowly reducing ferric chloride at elevated temperatures.[13] It did not affect the product with regard to color and thermal stability.

EXPERIMENTAL

Materials

Ethyl and butyl acrylate were oridinary polymerization-grade monomers, freed from inhibitor by an alkali-wash and dried on calcium chloride. Vinyl chloride was Fluka Puriss. Ethylene, propylene, and butene-1 were Matheson C.P. grade.

Diethyl maleate and diethyl fumarate were Fluka Purum products, distilled under vacuum before use. Carbon tetrachloride was a Frutarom analytical reagent.

Ferric chloride hexahydrate was from the Fisher Scientific Co., and triethylammonium chloride was Fluka Purum. Anhydrous cupric chloride was prepared from the dihydrate by heating at 200°C to constant weight. Isobutyraldehyde was freshly distilled, and benzoin was recrystallized from carbon tetrachloride before use (mp 137–138°). Ethanolamine was Eastman Kodak Whitelabel. The cosolvents acetonitrile, methanol, and ethanol were analytical grade.

Procedure

Cotelomerizations of vinyl chloride with acrylate, fumarate, and maleate esters were carried out in sealed glass ampoules. A solution containing all the reaction components (according to Table I), except vinyl chloride, was cooled in a Dry Ice–acetone bath, and a known excess of vinyl chloride was dissolved in it. The solution was then transferred to a precooled ampoule fitted with a stopcock and containing a boiling chip. After slowly warming, excess vinyl chloride was cautiously boiled off, completely expelling the air from the system. The stopcock was closed, and after cooling again to −70°C, the ampoule was sealed and then heated in a constant-temperature oven. At the end of the reaction, the ampoule was cooled again in acetone–Dry Ice, opened, and unreacted vinyl chloride was boiled off. The solution was then washed three times with 1*N* aqueous hydrochloric acid until free of iron, followed by water until neutral, and then dried on calcium chloride. Volatiles were removed by distillation and finally pumped out for $^1/_2$ hr at 0.1 mm pressure and 110°C in a rotatory film evaporator. The product was generally a viscous, colorless or slightly colored liquid.

When the comonomer was an acrylate ester, 3 ml of a methylene chloride solution that was 0.04*M* in (anhydrous) cupric chloride and 0.06*M* in triethylammonium chloride was added after boiling off excess vinyl chloride. This was found necessary in order to prevent polymerization of acrylate during the subsequent stripping operations (finally at 70° and 0.1 mm, during $^1/_4$ hr). The residue was redissolved in methylene chloride, extracted with 1*N* hydrochloric acid until free of metal, and freed of solvent as described above.

For cotelomerization with ethylene, propylene, and butene-1, a glass-lined autoclave was used. The reaction mixture, excepting the monomers, was made up according to Table I, and then the autoclave was cooled in ice. Excess vinyl chloride was pressed in under magnetic stirring, and the excess was released in order to expel air. Subsequently, the olefin was introduced. The autoclave was then heated as indicated. After cooling to room temperature and release of gaseous olefins, the contents of the autoclave were treated as described above.

Ethylene–vinylchloride cotelomers produced with the modified amine–iron chloride system (see below) were nearly colorless after the reaction, but were discolored during the stripping operations. The color could be removed by bringing a concentrated solution of the product in carbon tetrachloride on a silica gel column (Merck, 70–325 mesh ASTM), eluting with the same solvent until no more product came off, and stripping again. Only a small proportion of the cotelomer (of comparatively high molecular weight) was retained by the column. The same treatment also removed color from vinyl chloride–olefin cotelomers made with other recipes and improved their thermal stability.

Trichloromethyl Affinity Ratios

Vinyl chloride, ethyl acrylate, and carbon tetrachloride (0.2 mole each) were heated in a sealed ampoule with 8 mmole anhydrous cupric chloride and 16 mmoles triethylammonium chloride, dissolved in 20 ml acetonitrile. After 2 hr at 125°C, the reaction was interrupted. After cooling, the mixture was washed twice with 1*N* aqueous hydrochloric acid and dried on calcium chloride. The respective yields of the 1:1 adducts of carbon tetrachloride to vinyl chloride and ethyl acrylate were determined by GLC (using the *methyl* acrylate 1:1 adduct[3] as internal standard). The column was 2 ft long, with 10% SE-30 silicon rubber on Chromosorb, at 100°C and 60 ml helium/min. Of the charged monomers, 5.3 mole-% vinyl chloride and 8.5 mole-% ethyl acrylate were converted into 1:1 adduct, giving a trichloromethyl affinity ratio (vinyl chloride/ethyl acrylate) of 0.63 (at 125°C).

By replacing ethyl acrylate with an equivalent quantity of ethylene and using a 100-ml glass-lined autoclave as the reactor, the trichloromethyl affinity ratio (vinyl chloride/ethylene) was determined to be 3.27 (at 125°C).

Analytical

The cotelomers were characterized in the following way:

Chlorine content was determined by the Schöniger method.[14] Molecular weight was determined by vapor phase osmometry with a Hitachi-Perkin-Elmer Model 115 molecular weight instrument. Redistilled and dried ethyl acetate was used as solvent. From the chlorine content and the molecular weight, the composition of a cotelomer $CCl_3(VC)_n(M)_mCl$ could be calculated (VC stands for a vinyl chloride and M, for a comonomer unit). Cotelomers containing ethyl esters (acrylate, fumarate, maleate) allowed a direct determination of composition by NMR (using a Varian 60 MHz instrument), by relating the area under the methyl triplet of the ethyl group centered at $\tau = 8.70$ to the total proton absorption, which yielded n/m. Molecular weights calculated indirectly from n/m and chlorine content were in good agreement with the values from direct MW determinations.

Thermal stabilities were measured as loss of hydrochloric acid (w/w) when a sample of 0.2–0.5 g cotelomer was heated in a stream of dry argon at 180°C during 80 min. The evolved acid was absorbed in water and automatically titrated by a radiometer titrator.

Glass transition temperatures (T_g) were measured in a Perkin Elmer differential scanning calorimeter.

For the estimation of compatibility with PVC, we used the hot-stage microscope test of Agnostopoulos et al.[15] that gives a temperature range (T_m) during which the polymer dissolves in excess cotelomer.

RESULTS AND DISCUSSION

Trichloromethyl Affinity Ratios

Cotelomerization differs from copolymerization in that, as a consequence of the very low DP (in our case between 4 and 10), the relative affinities of the comonomers towards the chain-starting trichloromethyl radical will affect the composition of the cotelomer. The same is true for the difference in reactivity of the growing radical derived from one or the other monomer toward the chain transfer agent or, in our case, ferric chloride. Moreover, little is known about copolymerization reactivity ratios at 125°C, the reaction temperature of the present work. The published values[9] can serve therefore only as a rough approximation in the choice of a suitable comonomer.

The trichloromethyl affinity ratio of the vinyl chloride/ethyl acrylate system was determined by the competitive formation of 1:1 adducts with carbon tetrachloride under copper chloride catalysis. We assume that the change in the catalyst does not affect the relative reactivity of the monomers toward the trichloromethyl radical. The amount of adduct (formed to a low conversion) gave the required affinity ratio directly. The same procedure was followed for ethylene. The found values were: vinyl chloride/ethyl acrylate = 0.63; and vinyl chloride/ethylene = 3.27, both at 125°C. A comparison of the reactivity per double bond should take into account that, in contrast to ethyl acrylate, ethylene can be attacked at both ends of the double bond.

Vinyl Chloride–Acrylate Cotelomers

Table I summarizes the results of cotelomerizations of vinyl chloride with ethyl and butyl acrylate at 125°C. Since the acrylate enters into the cotelomer much more rapidly than vinyl chloride, the composition of the feed changes accordingly, especially with a large excess of vinyl chloride. Those reactions which were run to a rather high conversion gave cotelomers that were indeed richer in vinyl chloride and had a lower MW (compare run 241 and 630 with 631 and 580.)

In reactions with a vinyl chloride/acrylate ratio of 9 in the feed, distillable products were always formed. The proportion of volatiles increased with conversion and with the vinyl chloride/acrylate ratio of the initial feed and amounted sometimes (run 241) to as much as 27% of the total product. Over 90% of the distillate which was collected consisted of the lower (1:1 to 3:1) vinyl chloride–carbon tetrachloride telomers, the balance being the acrylate 1:1 adduct and mixed telomers. This demonstrates the much

TABLE I

Carbon Tetrachloride–Vinyl Chloride–Acrylate Cotelomers
$CCl_3(VC)_n(EA)_mCl$[a]

Run no.	VC/EA (molar)	$FeCl_3 \cdot 6H_2O$, mmole	Time, hr	Time, Yield, g	Cl, %	MW	n/m	Thermal stability, %	T_m, °C	T_g, °C
				Ethyl Acrylate Cotelomers						
596	15:1	2.6	2.5	4.8	52.6	702	4.3	0.13	137–9	—
578	12:1	2.6	2.5	13.6	53.0	642	4.0	0.16	136–9	—
594	9:1	2.6	2.5	8.9	48.0	661	2.5	—	136–9	—
633[c]	9:1	2.6	2.5	7.0	48.6	565	2.1	0.25	136–7	−38
631	9:1	5.2	1.0	5.0	48.1	520	1.7	0.06	132–3	−43
241	9:1	2.6	4.5	20.1	53.8	526	3.2	—	—	—
609	7:1	2.6	2.0	11.8	47.6	541	1.8	—	—	—
630	6:1	2.6	2.5	12.0	45.0	622	1.7	0.08	136–7	−40
580	6:1	2.6	1.0	2.0	33.2	955	1.0	—	—	—
612	5:1	2.6	1.5	9.8	37.9	718	1.1	—	—	—
				n-Butyl Acrylate Cotelomers						
601	15:1	2.6	2.5	11.8	50.7	539	3.1	—	—	—
602	12:1	2.6	2.5	5.0	44.1	654	2.2	0.35		
617	9:1	5.2	2.5	9.6	47.1	568	2.3	0.07	146–8	−64
618	9:1	10.4	2.5	21.6	52.5	404	2.0	0.10	136–7	−68
599	9:1	15.6	2.0	19.0	54.6	460	3.2	0.03	137–9	—

[a] Total monomers: 0.8 mole; carbon tetrachloride: 40 g (0.26 mole); initiator (isobutyraldehyde): 1.2 g (15.6 mmoles); triethylammonium chloride: 2 × (molar) $FeCl_3 \cdot 6H_2O$; acetonitrile: 20 ml; reaction temperature: 125°C.

[b] Evolved HCl, w/w.

[c] Without triethylammonium chloride.

higher reactivity of vinyl chloride-derived radicals toward ferric chloride in step (5).

An increased concentration of the catalyst should decrease the molecular weight of the cotelomers, steps (5) and (6). This is not apparent from the table, but the average molecular weight of the *total* product, including distillable telomers, must be taken into account. It was indeed found that for a given conversion, the proportion of volatiles increased with the catalyst concentration.

Thermal stabilities fluctuated, but were generally satisfactory and comparable to a good grade of chlorinated paraffin. We found the stability to be dependent on the initiating system; isobutyraldehyde gave much more stable products than f.i. benzoin.

Vinyl Chloride–Fumarate and Vinyl Chloride–Maleate Cotelomers

For a given molar ratio of vinyl chloride/comonomer in the feed, fumarate and maleate cotelomers were richer in vinyl chloride than the corresponding acrylate cotelomers, in accord with the published reactivity ratios.

In runs with maleate, unconverted monomer consisted of diethyl furmarate only, as evident from its singlet NMR signal of the ethylenic protons (at $\tau = 3.17$; the corresponding maleate singlet is at $\tau = 3.72$). Apparently, the major part of maleate ester enters into the cotelomer only after isomerization. Identical cotelomers are, of course, formed either from maleate or fumarate esters, but they enter into the cotelomer at different rates. Table II gives some of the results of our experiments with this system.

For a given ratio of incorporated comonomers, the fumarate or maleate cotelomers have a higher molecular weight than the corresponding acrylate cotelomers; they also have a higher T_m and T_g.

In the MW range of 500–600, the T_m and T_g values were comparable to those of ethyl acrylate cotelomer and vinyl chloride homotelomer. The maleate and fumarate cotelomers were, however, much more viscous.

Cotelomers of Vinyl Chloride with Propylene Butene-1 and Ethylene

Since it is known that the thermal stability of PVC is improved by the incorporation of even a small number of propylene units, cotelomerization of propylene with vinyl chloride was tried. Here, vinyl chloride is the more reactive monomer, and at least equimolar amounts of the aliphatic olefin in the feed were taken. Radicals derived from the olefins are much more reactive toward ferric chloride, step (5), than those of vinyl chloride; virtually only 1:1 adduct is obtained in their reaction with carbon tetrachloride under iron chloride catalysis.[3] An increased proportion of these olefins in the feed tends therefore to lower the average DP of the total product and consequently to increase the volatile fraction. With molar ratios between 4:1 to 1:1 of propylene/vinyl chloride, the total weight of 1:1 adducts with carbon tetrachloride amounted to at least the weight of

TABLE II
Carbon Tetrachloride–Vinyl Chloride–Diethyl Fumarate and Maleate Cotelomers
$CCl_3(VC)_n(DEF)_mCl$[a]

Run no.	VC/DEF (molar)	$FeCl_3 \cdot 6H_2O$, mmole	Time, hr	Yield, g	Cl, %	MW	n/m	Thermal stability, %	T_m, °C	T_g, °C
				Diethyl Fumarate, Reaction Temperature 125°C						
93	1:4	1.3	5	4.3	19.3	1192	0.48	0.22	>160	−20
47	3:1	0.7	3	6.4	30.8	1077	1.77	—	—	—
56	3:1	1.3	2	6.5	33.5	797	1.43	—	—	—
52	3:1	2.6	2	5.0	36.2	588	1.11	—	—	—
91	4:1	1.3	5	7.9	45.3	651	3.27	0.26	—	−21
143	9:1	1.0	7	2.5	39.2	819	2.48	0.28	137–47	−10
				Diethyl Maleate, Reaction Temperature 110°C						
	VC/DEM									
242	3:1	1.3	2	1.9	49.5	610	3.76	—	—	—
218	6:1	1.3	5	1.5	52.5	569	5.47	0.19	132–3	−48
219	6:1	2.6	5	1.8	53.5	510	5.06	—	—	—

[a] Total monomers: 0.4 mole; carbon tetrachloride: 20 g (0.13 mole); initiator (isobutyraldehyde): 0.1 g (1.3 mmoles); triethylammonium chloride 2 × (molar) $FeCl_3 \cdot 6H_2O$; ethanol: 10 ml.

TABLE III
Carbon Tetrachloride–Vinyl Chloride–Olefin Cotelomers
$CCl_3(VC)_n(CH_2CHR)_mCl$[a]

Run no.	VC/olefin (molar)	CCl_4, g	Yield, g	Volatile telomer, g	Cl, %	MW	n/m	Thermal stability, %	T_m, °C
				Propylene					
499	1:4	20	2.4	2.6	63.3	362	1.9	0.05	110–12
501	1:2	20	3.8	3.8	62.6	376	1.9	0.08	116–20
502	1:2	10	4.2	4.3	65.1	412	4.1	0.08	110–12
509	1:2	5	1.5	4.0	62.3	404	2.3	0.19	118–20
504	1:1	20	4.0	4.5	61.3	382	1.7	0.07	106–10
521	3:1	10	6.5	4.6	64.1	438	4.1	0.14	122–23
529	5:1	10	9.5	4.9	66.0	412	5.3	0.04	121–23
				n-Butene					
527	3:1	10	4.7	3.2	66.0	397	6.0	0.04	118–20
544	5:1	10	10.5	—	67.0	398	7.9	0.06	115–19

[a] Total monomers: 0.4 mole; initiator (isobutyraldehyde): 0.5 g (6.5 mmoles); $FeCl_3 \cdot 6H_2O$: 0.352 g (1.3 mmoles); triethylammonium chloride: 0.36 g (2.6 mmoles); acetonitrile: 20 ml; reaction temperature: 125°C; reaction time: 5 hr.

TABLE IV

Carbon Tetrachloride–Vinyl Chloride–Ethylene Cotelomers

$CCl_3(VC)_n(CH_2CH_2)_mCl$[a]

Run no.	VC/ ethylene (molar)	Initiator, mmoles	Temp., °C	Time, hr	Yield, g	Cl, %	MW	n/m	Thermal stability	T_m, °C	T_g, °C
569	5:1	aldehyde[b] 6.5	125	5.5	5.7	67.2	452	9.6	0.08	122–23	−43
598	4:1	"	110	8	2.9	66.0	400	3.1	—	114–15	−65
559	3:1	"	125	5	3.1	65.5	448	4.1	0.09	119–20	−60
673	2:1	"	70	60	1.4	66.4	400	3.4	—	—	—
642	2:1	benzoin 1.3	100	22	13.7	64.5	419	2.6	unstable[c]	110–12	−72

[a] Total monomers: 0.4 moles; carbon tetrachloride: 10 g (65 mmoles); $FeCl_3 \cdot 6H_2O$: 0.352 g (1.3 mmoles); triethylammonium chloride: 0.36 g (2.6 mmoles); Acetonitrile: 20 ml.

[b] Isobutyraldehyde.

[c] Treatment with alumina removed benzoin and much improved thermal stability (0.08%).

TABLE V
Carbon Tetrachloride–Vinyl Chloride–Ethylene Cotelomers
$CCl(VC)_n(CH_2CH_2)_mCl$[a]

Run no.	Initiator	mmole	Promoter	Monomers/ CCl_4 (molar)	Temp., °C	Time, hr	Yield, g	Cl, %	MW	n/m	Thermal stability, %	T_m, °C	T_g, °C
699	AIBN	3	—	1:1	60	5	1.4	59.6	737	3.9	—	—	—
705	AIBN	0.6	Fe	1:1	75	6	1.8	58.6	685	2.7	0.47	136–37	−42
678	EA	10[b]	Cu	1:1	60	3	5.0	58.4	572	1.9	0.80	131–33	−39
682[c]	EA	10	Cu	1:1	100	2	10.4	59.8	555	2.3	0.95	124–25	−44
723	EA	10	Fe	1:1	70	3	1.4	55.8	741	1.9	—	—	—
679	EA	5	Cu	1:1	60	3	3.0	60.6	473	1.8	0.98	130–33	−46
746	AIBN	0.6	—	3:1	70	12	3.2	56.4	632	1.7	0.98	148–50	−33
760	EA	10	—	3:1	100	24	4.3	56.9	593	1.6	—	144–46	−40
757	AIBN	0.6	Fe	3:1	70	13	1.8	55.7	702	1.8	2.50	147–48	−24
750	benzoin	0.6	Fe	3:1	70	24	1.0	54.3	664	1.4	2.08	140–42	−20
759	isobutyraldehyde	20	Fe	3:1	70	96	0.3	58.5	520	1.6	0.40	—	—
755	EA	10	Fe	3:1	70	4	1.5	56.1	925	2.8	1.50	144–46	−30
747	EA	10	Cu	3:1	70	3	5.0	58.0	536	1.6	2.10	132–33	−50
753I	EA	10	Cu	3:1	70	3	3.2	57.3	471	1.1	0.98	130–32	−54
753II[d]	EA	10	Cu	3:1	70	3	2.5	60.7	448	1.6	0.24	126–28	−64

[a] Total monomers: 0.2 mole; molar ratio vinylchloride/ethylene: 1:2; promoter $CuCl_2 \cdot 2H_2O$(Cu) or $FeCl_3 \cdot 6H_2O$(Fe): 0.1 mmole; methanol: 20 ml.

[b] Ethanolamine

[c] Solvent: *tert*-butanol.

[d] 753I, after treatment with silica.

produced cotelomer. About 70% of the volatiles consisted of 1,1,1,3-tetrachlorobutane, the propylene 1:1 adduct. The balance was made up of (mainly) 1,1,1,3,3-pentachloropropane (the vinyl chloride adduct) and higher telomers.

Butene-1 behaved in a similar way. Ethylene, on the other hand, gave less volatiles. Moreover, there was a larger proportion of the vinyl chloride 1:1 adduct.

The olefin cotelomers had a good thermal stability, and their T_m value was low, indicating that olefin units in the telomer did not affect the compatibility with PVC adversely. The results are summarized in Tables III and IV.

Cotelomerization with Ethylene, Catalyzed by Amine/Metal Chloride (Table V)

The radical chain reaction between aliphatic amines and carbon tetrachloride, which is strongly promoted by iron and copper salts, has been used in our laboratory as an initiating system for the telomerization of ethylene and carbon tetrachloride.[10] The distribution of the telomers ($CCl_3(CH_2CH_2)_nCl$; $n = 1–5$) was found to be essentially identical with that obtained with the conventional initiators, benzoyl peroxide or azobisisobutyronitrile (AIBN). With these catalysts, vinyl chloride gives telomers with a much higher average DP.[2] It was therefore of interest to try the amine system on the combination ethylene/vinyl chloride. The reactions turned out to be much faster than those catalyzed by iron chloride only.

A shift toward higher DP's was evident from the much diminished amount of volatile telomers. By changing the reaction temperature and the molar ratio of total monomer/carbon tetrachloride, the MW could be varied in the range 450–900. Again, a higher proportion of ethylene in the feed gave a product with a lower molecular weight.

Ethylene as cotelomer appears to be able to depress the MW also in the absence of any metal ion or amine; with AIBN as the only catalyst, and a molar ratio ethylene/vinyl chloride of 2:1, a cotelomer with MW 630 was obtained at 60°C. Homotelomerization of vinyl chloride under the same conditions gave a MW of 2720.

The high MW cotelomers are still liquid. Like acrylate and fumarate esters, incorporated ethylene thus appears to extend the liquid range of the telomers.

The products of reactions catalyzed by amine/ferric chloride are initially colorless but discolor to light brown during stripping. Treatment with silica gel gives a colorless product with an improved thermal stability.

Glass Transition Temperature of the Cotelomers

Our results indicate that the MW is the most important single factor which affects the T_g of the neat cotelomer, irrespective of the nature of the comonomer.

Since there is no simple relationship between T_g of the neat plasticizer and its efficiency in polymer–plasticizer compounds, we cannot deduce much from T_g values alone about the performance (flexural modulus, low-temperature properties, impact strength, etc.) of the various cotelomers as plasticizers for poly(vinyl chloride).

We intend to publish information about these properties separately.

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