

A New Strategy for Plasticizing and Stabilization of PVC Mixtures

Radka Kalousková, Helena Fartáková, Lenka Malinová, Jiří Brožek

Department of Polymers, Institute of Chemical Technology, Prague, 166 28 Prague 6, Czech Republic

Correspondence to: R. Kalousková (E-mail: radka.kalouskova@vscht.cz)

ABSTRACT: This study was undertaken to examine possible use of classic tetravalent tin-based heat stabilizers for the preparation of a polymer plasticizer: poly(ϵ -caprolactone) (PCL) and simultaneous stabilization of PVC in PVC/PCL mixtures. PCL was prepared from ϵ -caprolactone (CL) by polymerization initiated by tin-containing organic compounds and successfully used to simultaneously plasticize and stabilize PVC. Moreover, conditions under which the polymerization of CL took place directly *in situ* during PVC/CL mixture processing were found. The procedure yielded homogeneous plasticized PVC/PCL mixtures, which were stable and contained >90% of the original monomer content. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41066.

KEYWORDS: degradation; plasticizer; polyesters; poly(vinyl chloride); ring-opening polymerization

Received 22 January 2014; accepted 27 May 2014

DOI: 10.1002/app.41066

INTRODUCTION

With its nearly eighty-year-old history of industrial production, polyvinylchloride (PVC) is one of the oldest synthetic polymeric materials. Good availability of its monomer and suitable properties of the polymer—easy processing, chemical resistance, fire-resistance, ability to gelatinize with plasticizers, good miscibility with a number of additives, etc.—are the features, which ensure pvc a wide spectrum of use. However, some PVC additives (examples include some specific stabilizers, plasticizers, etc.) are considered questionable as far as health and/or environment is concerned. However, heat stabilizers are indispensable for PVC thermal processing as they at least partially prevent its thermal degradation and react with eliminated hydrogen chlorine. The use of lead-based stabilizers has been in decline, while mixed stabilizers on the basis of calcium/zinc and tetravalent tin-based organic compounds are frequently used.¹

For years, phthalic acid esters (mostly di-(2-diethylhexyl)phthalate) had been the most effective and therefore the most widely used plasticizers. Since low-molecular phthalates were classified by the EU as reprotoxic compounds, demand for plasticizers has shifted to phthalates with higher molecular weight [di-(2-propylheptyl)phthalate, diisononylphthalate, diisodecylphthalate] and plasticizers with more favourable classification.² However, it is not easy to find compounds, which could substitute di-(2-diethylhexyl)phthalate while retaining all the desired properties of plasticized PVC mixtures.

Low-molecular polymer plasticizers offer a possible solution to the problem. This is not a new idea, as the properties of PVC blended with other polymers have been studied for decades. In

the last few years, research has been focused on mixtures with polyesters on the basis of adipic acid, azelaic acid, phthalic acid, sebacic acid fatty acids, etc.³ The miscibility of PVC with polyesters is a result of specific interactions between the carbonyl group of the polyester and α -hydrogen on the PVC chain and therefore depends on the ratio of the methylene and carbonyl groups in the repetitive unit of the polyester. It is poly(ϵ -caprolactone) (PCL) that offers the ideal methylene/carbonyl group ratio ($\text{CH}_2/\text{CO} = 5$) and a suitable interaction parameter.^{4–6} PCL is biodegradable, nontoxic, semicrystalline polyester with glass transition temperature -60°C and melting temperature 60°C . PCL is miscible with chlorinated polymers, decreases their glass transition temperature and is an effective plasticizer.⁷

Preferred strategy for PCL preparation is the polymerization of ϵ -caprolactone (CL) with ring opening. PCL can be prepared by using a variety of anionic, cationic, or other coordination initiators. Each method affects the resulting molar mass, molar mass distribution, end group composition, and chemical structure of polymers.⁸ In the presence of organometallic compounds, CL polymerization takes place via coordination-insertion mechanism and may be accompanied by undesirable transesterification reaction depending on particular conditions.⁹ Aluminum trialkoxides, dialkylaluminum alkoxides, and initiators of more complicated structures are used for controlled PCL synthesis.^{10–13} Zinc and/or tin based organometallic compounds are the most frequently used polymerization initiators. However, the carboxylates these metals are considered as catalysts rather than an initiators and polymerization in the present of tin 2-ethylhexanoate when cointiator (mostly alcohol) is absent, is very slow.^{9,14–16} Sometimes also tetravalent tin compounds

(dibutyltin dioctoate and dibutyltin dilaurate) have been used as polymerization initiators.^{17–19}

Tetravalent tin organic compounds which are the main component of classic PVC stabilizers were used in this study for simultaneous preparation of PCL and thermal stabilization of PVC in plasticized PVC/PCL mixtures.

EXPERIMENTAL

Materials

PVC Neralite 682 – suspension type, $K_h = 68$, was kindly supplied by Spolana Neratovice. The thermal stabilizer Tinstab BM 360 (di-*n*-butyltin maleate) purchased from Akros Chemicals, GB. Lubricant Bralen SA 200-22 (LDPE) (Slovnaft, the Slovak Republic) was added in the amount of 1.0 g/100 g PVC.

ϵ -Caprolactone (CL) (Fluka) was dried by CaH_2 and distilled under reduced pressure. Initiators dibutyltin(IV) maleate and dibutyltin dilaurate (95%) were purchased from Sigma-Aldrich. *n*-Butanol and hexane-1,6-diol were supplied by Merck.

Preparation of PCL

PCL was prepared by the polymerization of CL initiated by dibutyltin(IV) maleate or dibutyltin dilaurate (1.0 mol %) at temperatures 130–170°C, adapted according to Ref. 8. An initiator, CL, and/or a coinitiator were introduced under a stream of argon into a flask. The reaction batch was stirred and heated to expedite its dissolution and subsequently transferred into 1 g ampoules. PCL to be used as PVC plasticizer was prepared in 15 g ampoules in a similar manner.

Preparation of PVC/PCL or PVC/CL Mixtures

Mixtures in the form of foils 0.4 mm thick were prepared on a Polymix 80T two-roll mill, roller size 80/300 mm, slip 1.2 (rotation velocity ratio 22 : 19). Rolling temperature $160 \pm 0.1^\circ\text{C}$, mixture preparation time 5 min. Specimens (thickness 0.4–0.7 mm) were obtained by 3 min compression at 195°C and 30 MPa.

Procedures

Number-average molar mass (M_n) of PCL was determined by size exclusion chromatography (SEC) using the Waters Breeze system with multitasking dispersal detector (analyzer) (MALLS, minidawn trees, Wyatt) with laser wavelength 658 nm (Waters 2410 28), refractive index, Waters 1515 pump, Waters 717+ autosampler and column thermostat, the refractive index increments dn/dc of chloroform solutions of PCL were $0.060 \text{ cm}^3/\text{g}$.²⁰

The yield of polymer was determined gravimetrically by extraction of the polymerization product (polymerizate) with methanol extraction (three-times for 60 min at laboratory temperature). The amount of PCL and unreacted CL in the PVC/PCL mixtures were determined by ^1H NMR spectroscopy (Bruker 600 Avance, trichannel digital NMR spectrometer).

HCl eliminated from PVC mixtures was quantified by a continuous potentiometer.²¹ Thermal stability (TS) values were read from the kinetic curves obtained for individual mixture. The TS value represents the time period (in minutes) from the start of heat treatment to the moment of a rapid increase of the amount of liberated HCl. The color stability of the blends in

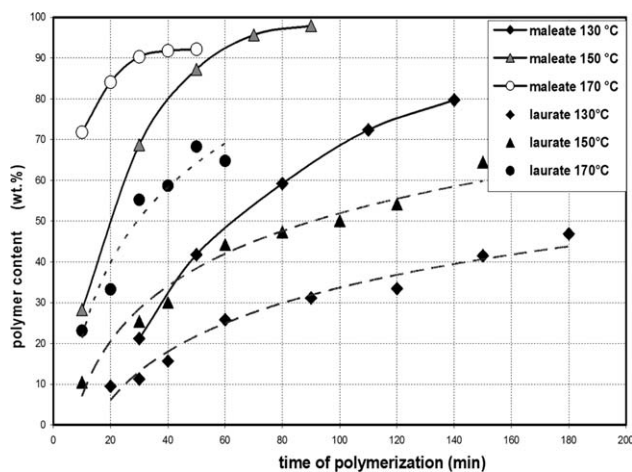


Figure 1. The dependence of PCL content (determined by methanol extraction of the polymerizate) on the time of CL polymerization initiated by 1 mol % dibutyl tin maleate (solid line) and 1 mol % dibutyl tin dilaurate (dash line).

the foils treated at 180°C in air using TESTER TOM Model 204 was evaluated visually.

DMA measurements were performed using DMA DX04T tester (RMI, Czech Republic), in a temperature range between -50 and 120°C at a heating rate of 3°C min^{-1} ; bending mode Single Cantilever with constant deformation of $\pm 0.2 \text{ mm}$ and sinusoidal force at the frequency of 1 Hz was used. Glass transition temperature was determined from the maxima of the dissipation component of dynamic modulus of elasticity.

RESULTS AND DISCUSSION

The study was undertaken to examine various possibilities to plasticize and stabilize PVC/PCL mixtures. First, the course of CL polymerization in monomeric phase initiated by organotin compounds used for PVC stabilization was studied. Samples of synthesized PCL were used to plasticize and stabilize PVC (PVC/PCL mixtures). Subsequently, efforts were made to determine suitable conditions for CL polymerization initiated by organotin compounds during the processing of PVC and monomer CL mixtures (PVC/CL mixtures). The mixtures were prepared by melt blending to emulate production conditions.

Polymerization of CL Initiated by PVC Stabilizers

PCL was prepared by monomer CL polymerization initiated by dibutyltin maleate and dibutyltin dilaurate (1 mol %) at the temperatures 130, 150, and 170°C . The CL polymerization temperatures were chosen taken into account PVC processing temperatures. Used concentration of the initiator provides required molar weight of PCL (polymeric plasticizer). In addition, the plasticizer prepared in this way contains sufficient amount of Sn compound needful for stabilization of PVC/PCL mixture.

The results show that polymer content increased with the temperature and time of the polymerization (Figure 1). The dibutyltin maleate-initiated polymerization was faster and yielded higher conversion levels. The addition of *n*-butanol as a coinitiator (in the ratio 2 : 1 v/v initiator : coinitiator) into polymerization batch slightly increased the reaction rate (Table I).

Table I. Characterization of PCL Samples in 1 g Ampoules Prepared by CL Polymerization Initiated by 1 mol % Organotin Initiator

Initiator/stabilizer	Temperature (°C)	Time (min)	y_w (%)	M_n (kg/mol)	M_w (kg/mol)	\bar{D}
Dibutyltin maleate	130	50	42	4.9	5.2	1.06
		140	80	8.4	10.1	1.20
	150	10	28	3.7	3.9	1.05
		70	96	10.3	12.9	1.25
Dibutyltin maleate : butanol 2 : 1	130	30	28	2.8	2.9	1.04
		60	61	5.0	5.5	1.09
Dibutyltin dilaurate	130	90	31	8.9	13.1	1.47
		210	51	9.9	18.1	1.83
	150	40	30	17.6	27.0	1.53
		150	68	12.4	28.5	2.30
Tinstab BM 360	130	40	19	2.6	2.8	1.09
		60	37	2.8	3.0	1.06

y_w : gravimetric conversion (determined by methanol extraction of the polymerize); M_n : number average molar mass of the polymer; M_w : mass average molar mass of the polymer; \bar{D} : dispersity (M_w/M_n ratio).

Molar masses of the polyester prepared in the presence of dibutyltin maleate increased with polymerization temperature and time, and slight increase of dispersity was observed at higher conversion levels (Table I). The addition of the coinitiator had no influence on the molar mass of PCL prepared.

Temperature had a considerable effect on the course of CL polymerization initiated by dibutyltin dialurate. Number average molecular mass (M_n) decreased and dispersity increased after 150 min at 150°C as a result of side reactions (intermolecular and intramolecular transesterifications). The reactions are known to generate linear and cyclic oligomers at higher temperatures and prolonged polymerization time.⁹ It is apparent that the structure of the initiator (maleate vs. dilaurate) fundamentally influenced the course of the polymerization process and the properties of its product. The results show that organotin compounds used to stabilize PVC can be successfully used to initiate polymerization of CL.

However, heat stabilizers used to stabilize PVC are not pure compounds but contain various additives, which increase the efficacy of the main component, improve compatibility with PVC, reduce the price of stabilizer, etc. Therefore, a commercially available dibutyltin-maleate-based heat stabilizer Tinstab BM 360 was also tested. The polymerization was much slower in comparison with “pure” maleate and the molar mass of the PCL obtained was significantly lower (Table I).

PVC/PCL Mixtures

For the purpose of PVC plasticizing and stabilization, polymerizates with various PCL content were prepared in 15 g ampoules by dibutyltin maleate-induced CL polymerization (polymerizate denotes the nonextracted product of CL polymerization—a mixture comprising the polymer, low-molecular fractions, residual monomer, and the catalyst). The PCL-A polymerizate was polymerized at the temperature 150°C for 10 min ($y_w = 16\%$, $M_n = 3.2$ kg/mol) and the PCL-B polymerizate at the same temperature but for 70 min ($y_w = 95\%$, $M_n = 10.1$ kg/mol). The difference in polymer yield and M_n after 10 min of polymerization in

the 1 and 15 g ampoules was due to slower heating of the greater volume of the reaction mixture in the large ampoules.

The polymerizates PCL-A and PCL-B were mixed with PVC in quantities 20 and 40/100 g PVC (16.4 and 28.5% w/w) on two-roll mill and pressed. Specimens prepared that way were used to evaluate thermal and color stability, thermal properties and to determine the content of plasticizer in the polymers (Table II).

Thermal stability (TS) of a mixture is the time during which the stabilizer effectively neutralizes HCl generated by thermal degradation of PVC (dehydrochlorination) preventing thus HCl to eliminate from the mixture. Table II gives the TS values of PVC and PVC/PCL mixtures, respectively, and Figure 2 shows the dehydrochlorination curves of the mixtures and stabilized or “pure” PVC. Stabilization effects of the “pure” dibutyltin maleate and commercial stabilizer (Tinstab BM 360) in the mixtures of nonplasticized PVC were more or less comparable and increased linearly with stabilizer content (Table II). Figure 2 and Table II prove that PVC was effectively stabilized also by the polymerizates containing the above-mentioned organometallic compounds (CL polymerization initiators).

At the dose of 20 g polymerizate/100 g PVC, the resulting mixture contained 0.6 g of dibutyltin maleate (as the initiator) and this quantity ensured good TS (44 min) of the mixture. This value is approximately by 1/3 lower than the TS of pure PVC stabilized by the same amount of Tinstab BM 360 (64 min). A similar decrease of TS was observed in the PVC/PCL mixtures stabilized by the same quantity of tetravalent tin-based stabilizer in which PCL was prepared by CL polymerization initiated by another initiator type, for example, ethylmagnesium bromide.²² We assume that the weaker stabilization effect of dibutyltin maleate is not related to its role as the CL polymerization initiator but is caused by competitive interactions of the polyester in the areas where PVC is stabilized by the tin-based stabilizer.^{23–25} Moreover, also mechanic stress during the processing of PVC/PCL mixtures undoubtedly caused stabilizer consumption, thus reducing the dehydrochlorination induction period. The above-

Table II. The Composition of PVC/Polymerizate Mixtures (in g/100 g PVC)

Polymerizate	Amount of polymerizate (g/100 g PVC)	Amount of stabilizer (g/100 g PVC)	m_{CL} (g/100 g PVC)	m_{PCL} (g/100 g PVC)	w (% w/w)	TS (min)	T_g (°C)
-	0	0.6	-	-	-	64	90
-	0	0.6 ^a	-	-	-	65	89
-	0	1	-	-	-	89	89
-	0	1 ^a	-	-	-	92	89
-	0	1.5	-	-	-	120	92
PCL-A	20	0	-	-	-	44	70
PCL-A	20	1	0.9	8.3	46	112	68
PCL-A	40	1	2.4	13.6	40	129	51
PCL-B	20	0	-	-	-	42	44
PCL-B	20	1	0	19.6	98	119	45
PCL-B	40	1	0	35.6	89	130	20

The mixtures contained 100 g PVC; 0, 20, and 40 g polymerizate; 1 g lubricant and 0–1.5 g thermal stabilizer Tinstab BM 360.

^aStabilizer dibutyltin maleate; m_{CL} , m_{PCL} – CL and PCL content after mixture processing determined by ¹H NMR; w – CL and PCL content in PVC/polymerizate mixture expressed as fraction from total quantity added; TS: thermal stability of PVC/polymerizate mixtures; T_g : glass transition temperature measured by DMA

mentioned conclusions are also supported by the results of the evaluation of thermal color stability (Figure 3, mixtures Nos. 1–4). Generation of polyene sequences could be observed after about 25 min of thermal stress, which was manifested by pronounced coloration of the PCL-containing mixtures though the initiator/stabilizer was not yet exhausted and continued to neutralize arising HCl. Figure 3 shows also the behavior of a mixture stabilized by tin(II) 2-ethylhexanoate, a classical CL polymerization initiator; the compound had obviously significantly lower stabilization effect on PVC (Figure 3, mixture No. 7).

All the mixtures studied were homogenous with only one glass transition temperature (T_g). In case of nonplasticized PVC

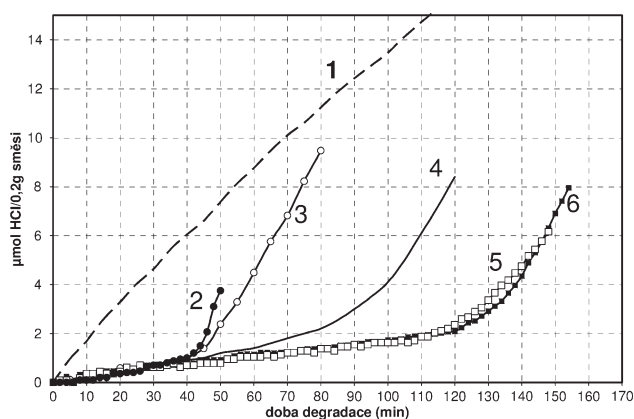


Figure 2. The dependence of released HCl on the time of mixture degradation (continuous potentiometric titration, 180°C, air). Mixture composition (in g/100 g PVC): 1: unstabilized PVC; 2: PVC/20 g PCL-B polymerizate; 3: PVC/20 g PCL-A polymerizate; 4: stabilized PVC (1 g Tinstab BM 360); 5: stabilized PVC/40 g PCL-B polymerizate; 6: stabilized PVC/40 g PCL-A polymerizate.

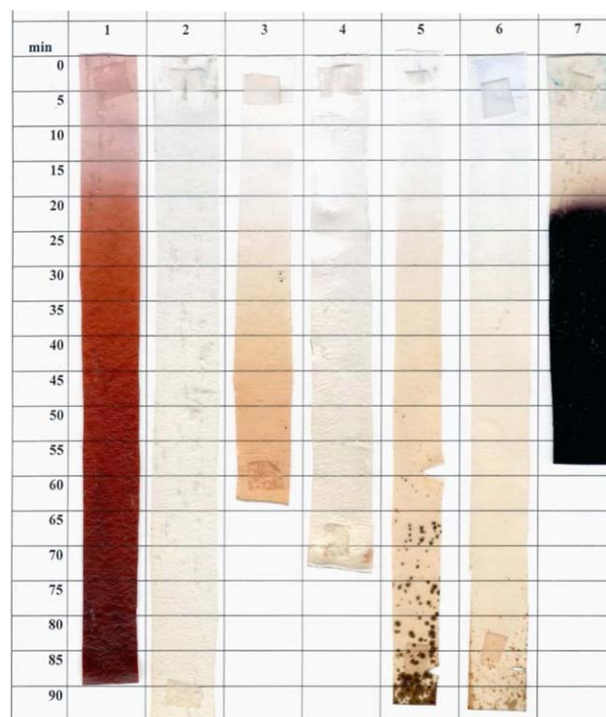


Figure 3. Thermal color stability of various mixtures (180°C, air). Mixture composition: 1: PVC/CL without stabilizer/initiator; 2: PVC/stabilizer Tinstab BM 360 (1 g/100 g PVC); 3: PVC/PCL-A (20 g/100 g PVC); 4: PVC/PCL-A (20 g/100 g PVC) stabilized by Tinstab BM 360 (1 g/100 g PVC); 5: PVC/CL-preheated (130°C/60 min, 20 g CL/100 g PVC, 1 g dibutyltin maleate/100 g PVC); 6: PVC/CL-preheated (170°C/10 min, 40 g CL/100 g PVC, 1 g dibutyltin maleate, and 1 g hexanediol/100 g PVC); 7: PVC stabilized by tin(II) 2-ethylhexanoate (1 g/100 g PVC). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

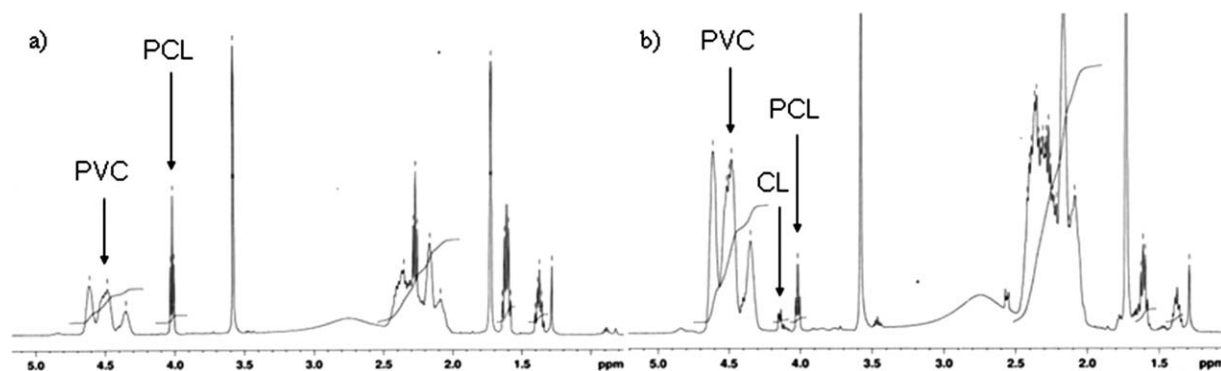


Figure 4. ^1H NMR spectrum of the PVC/PCL-B mixture (a) and PVC/CL mixture (b).

mixtures, its value was around 90°C (Table II). The addition of a polymerizate decreased the T_g of relevant PVC/polymerizate. The content of PCL in the polymerizate added significantly influenced the T_g decrease. The presence of polyester and CL, respectively, in PVC/polymerizate mixture was detected by ^1H NMR. Figure 4(a,b) show an integrated trace of a PVC/polymerizate mixture; the peak in the 4 ppm region belongs to the CH_2 group next to $\text{C}=\text{O}$ in PCL, the one in the 4.15 ppm region to the same group in CL, and the peak in the 4.5 ppm to the CH group in PVC. PCL or CL content, respectively, in all specimens was calculated from the areas under the peaks. Over 90% of the added polymerizate remained bound in the PVC/PCL-B mixtures [Figure 4(a)]. In case of the mixtures with PCL-A (low PCL-content in polymerizate), there was a massive loss of the monomer and low-molecular fractions during thermal processing; as a result, less than a half of the original content of the plasticizer and monomer remained bound in the PVC/PCL-A mixtures. The result was a significantly lower softening effect of PCL and much higher T_g of the PVC/PCL mixtures.

PVC/CL Mixtures

The incorporation of PCL into PVC mixture and therefore PCL softening effect are undoubtedly related to the properties of the polyester (the content of crystalline phase, chain branching, molar mass) and to the method employed to prepare the mixture. The above-mentioned polymerization tests (Section “Polymerization of ϵ -caprolactone initiated by PVC stabilizers”) suggested that CL polymerization initiated by organotin

compounds used as PVC stabilizers might be feasible. In the next stage, therefore, attempts were made to achieve *in situ* CL polymerization initiated by dibutyltin maleate (PVC stabilizer), that is, CL polymerization during the course of PVC blend processing, thus performing PVC stabilization and plasticizing as a one-step operation.

In the first step, individual mixture components, that is, PVC, CL, the stabilizer/initiator and lubricant were mixed together and processed on two-roll mill (Table III). The mixtures typically lost some 10–12% of their mass. Assuming that the mass loss was solely due CL losses, some 30–40% of the original CL remained firmly incorporated in the PVC/CL mixtures. This is also confirmed by the results of ^1H NMR determination. After processing, PVC/CL mixtures contained 30–40% of the original quantity of CL in its polyester and monomer forms, with PCL/CL ratio about 2 : 1 [Figure 4(b), Table III]. Also the value of T_g 75°C (Table III) is in line with the plasticizer content in the after the addition of 20 g of CL. Preheating of a PVC/CL mixture (120°C , 1 h) prior processing did not significantly alter PCL content in the mixture.

In the second step, CL plus the initiator/stabilizer and coinitiator, if any, were mixed together and the mixtures were kept at the temperatures 130 – 170°C for a period from 10 to 60 min. The initiator was added in standard quantities used to stabilize PVC, that is, 1/100 g PVC (Table IV). Polymerization, which took place at the temperatures 150°C and 170°C , respectively, for the time indicated yielded CL polymerizates containing more than 2/3 of PCL with M_n about 4 kg/mol and relatively

Table III. Composition and Characterization of some Mixtures PVC/CL (the Mixtures Contained 100 g PVC, 10–40 g CL, 0–1 g Dibutyltin Maleate as Initiator and Stabilizer, 1 g Lubricant)

Amount of CL at the beginning (g/100 g PVC)	Dibutyltin maleate (g/100 g PVC)	m_{CL} (g/100 g PVC)	m_{PCL} (g/100 g PVC)	w (% w/w)	TS (min)	T_g ($^\circ\text{C}$)
10	1	1.6	2.4	40	–	83
20	0	4.6	–	27	74	77
20	1	2.6	4.2	34	75	75
20 ^a	1	2.6	4.8	37	78	74
40	1	9.2	6.0	38	–	58

^aThe mixture was preheated ($120^\circ\text{C}/1$ h) prior processing; m_{CL} , m_{PCL} – CL, and PCL content after processing determined by ^1H NMR; w: fraction of CL and PCL incorporated in the mixture from added CL; TS: thermal stability of PVC/CL mixtures; T_g : glass transition temperature.

Table IV. Conditions Used to Prepare PVC/CL Mixtures and the Characteristics of Individual Polymerizates and PVC/CL Mixtures

Temperature/time of preheating (°C/min)	Initiator/stabilizer (g/100 g PVC)	y_w (%)	M_n (kg/mol)	\bar{D}	Amount of polymerizate after preheating (g/100 g PVC)	m_{PCL} (g/100 g PVC) determined by		w (% w/w)	TS (min)	T_g (°C)
						Gravimetry	NMR			
130/60	1 ^a	29	2.9	1.04	20	-	15.6 ^b	78	68	54
	1 ^c	20	2.9	1.04	20	17.5	18.0 ^b	88	72	47
	2 ^c				40	34.3	35.4	89	120	20
	1 ^c	18	2.9	1.04	40	24.6	24.6 ^b	61	65	35
150/30	1 ^c	72	4.3	1.11	20	13.0	13.5	93	-	52
170/10	1 ^c	70	4.3	1.21	20	17.6	17.6	88	82	47
	2 ^c				40	23.6	30.3	76	115	28
	1 ^d	61	3.9	1.13	20	19.5	19.5	98	75	42
	2 ^d				40	37.1	37.7	94	100	14

y_w : gravimetric conversion (determined by methanol extraction of the polymerizate); M_n : number average molar mass of the polymer; \bar{D} : dispersity (M_w/M_n ratio); m_{PCL} : PCL content after blend processing determined by gravimetry and ¹H NMR; w : fraction of CL and PCL incorporated in the mixture from added CL; TS: thermal stability of PVC/CL mixtures; T_g : glass transition temperature.

^aStabilizer of PVC Tinstab BM 360.

^bThe PVC/polymerizate mixture contained also CL in quantities 0.5–2 g.

^cDibutyltin maleate.

^dDibutyltin maleate and hexandiole as coinitiator (1 : 1).

narrow distribution. Mixture mass loss during blending was negligible (max 2% w/w).

A lubricant and PVC were added to the above-mentioned polymerizate in pertinent quantities so that the mixture to be processed contained 20 g (i.e., 16.4% w/w), or 40 g of the plasticizer per 100 g PVC (i.e., 28.5% w/w; Table IV). The mixtures were mixed, processed on the two-roll mill, pressed and their TS, thermal properties, and plasticizer content in the polymer were evaluated.

Again, TS of the PVC/CL mixtures were by about 1/3 shorter in comparison with stabilized nonplasticized PVC. The development of thermal color stability (Figure 3, mixtures Nos. 5 and 6) was comparable with the mixture containing the tin (IV)-based stabilizer and PCL. In addition to the above-mentioned reasons is important to mention that CL itself accelerates the dehydrochlorination of unstabilized powder PVC, increasing the rate of HCl eliminate from PVC from 16.4 to 23.3 $\mu\text{mol}/0.2$ g PVC.²³ When CL content in PVC/CL mixture was increased to 40/100 g at the same stabilizer/initiator concentration, TS of the mixture was shortened by about one tenth (Table IV), which also documents the negative effect of CL.

In this case, T_g values of the PVC/CL mixtures were significantly lower, which can be explained by higher conversion level of the monomer to PCL during mixture processing and, thus, its higher content in the processed mixture (Table IV). Polymerizate content in the mixtures was again determined from ¹H NMR spectra or by gravimetry and the results are relatively compatible. It is evident that CL polymerization took place not just when the monomer/initiator mixture was heated but also during subsequent PVC processing. As a result, the PVC/CL

mixtures retained as much as 98% of the added CL depending on the initiator content and/or the presence of the coinitiator in the preheated mixture, temperature employed, and the length of the mixing period of the components. T_g of the mixtures linearly decreased with increasing polymerizate content (Figure 5). The PVC/CL mixture with CL polymerized by the initiator/coinitiator combination displayed the lowest T_g value (14°C) and the mixture retained 94% of added CL (Table IV). In this case, the PVC softening effect was at least comparable with the effect of low-molecular commercial plasticizers. The following T_g values for individual plasticizers added in the same quantities of 25 g per 100 g PVC were found: Hexamoll DINCH 12°C, DOP 28°C, and TXIB 58°C.

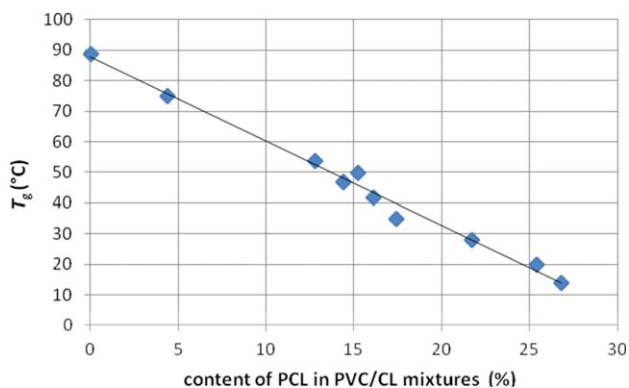


Figure 5. The dependence of glass transition temperature of PVC/CL mixtures on plasticizer content in the mixtures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSION

A new strategy for the plasticizing and stabilization of PVC mixtures, which would allow to perform PVC stabilization and plasticizing as a one-step operation was successfully examined and found feasible. PCL prepared by the CL polymerization initiated by tin(VI) organometallic compounds was used as a plasticizer and stabilizer of PVC mixtures. Mixture preparation was made easier as it was feasible to initiate CL polymerization by the above-mentioned compounds *in situ*, that is, during PVC/CL mixture processing. The procedure yielded homogenous and stabilized PVC mixtures plasticized by PCL, the effectivity of which was found comparable to that of low-molecular plasticizers. The double role (i.e., the initiator and the stabilizer) of the organotin compound examined did not markedly influenced TS of the mixtures.

ACKNOWLEDGMENTS

The research was supported by the research programme MSM 6046137302. The work of Dr. Jan Merna on SEC measurements is greatly acknowledged.

REFERENCES

1. Wypych, G. In *PVC Degradation & Stabilization*; ChemTec Publishing: Toronto, **2008**.
2. Plasticizer and flexible PVC information centre. Available at: http://www.plasticizers.org/en_GB/regulation/reach. Accessed on November 27, **2013**.
3. Wypych, G. In *Handbook of Plasticizers*; ChemTec Publishing: Toronto, **2012**.
4. Chiu, F.-C.; Min, K. *Polym. Int.* **2000**, *49*, 223.
5. Woo, E. M.; Barlow, J. W.; Paul, D. R. *Polymer* **1985**, *26*, 763.
6. Ziska, J. J.; Barlow, J. W.; Paul, D. R. *Polymer* **1981**, *22*, 918.
7. Shi, G.; Cooper, D. G.; Maric, M. *Polym. Degrad. Stab.* **2011**, *96*, 1639.
8. Malinová, L.; Brožek, J. *Polym. Bull.* **2014**, *71*, 111.
9. Albertsson, A.-C.; Varma, I. K. *Biomacromolecules* **2003**, *4*, 1466.
10. Dubois, P.; Jérôme, R.; Teyssié, P. *Makromol. Chem. Macromol. Symp.* **1991**, *42*, 103.
11. Duda, A.; Penczek, S. *Macromol. Rapid Comm.* **1995**, *16*, 67.
12. Miola-Delaite, C.; Hamaide, T.; Spitz, R. *Macromol. Chem. Phys.* **1999**, *200*, 1771.
13. Moriya, O.; Matsui, A.; Sugizaki, T.; Oikawa, M.; Kageyama, T.; Nakamura, Y.; Endo, T. *Polym. J.* **2000**, *32*, 82.
14. Leenslag, J. W.; Pennings, A. J. *Makromol. Chem.* **1987**, 188, 1809.
15. Penczek, S.; Duda, A.; Kowalski, A.; Libiszowski, J.; Majerska, K.; Biela, T. *Macromol. Symp.* **2000**, *157*, 61.
16. Storey, R. F.; Taylor, A. E. *J. Macromol. Sci. Chem.* **1998**, *35*, 723.
17. Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **2000**, *33*, 689.
18. Möller, M.; Kange, R.; Hedrick, J. L. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 2067.
19. Price, G. J.; Lenz, E. J.; Ansell, C. W. G. *Eur. Polym. J.* **2002**, *38*, 1753.
20. Wu, C.; Woo, K. F.; Xiaolie, L.; Ma, D.-Z. *Macromolecules* **1994**, *27*, 6055.
21. Vymazal, Z.; Czakó, E.; Meissner, B.; Štěpek, J. *J. Appl. Polym. Sci.* **1974**, *18*, 2861.
22. Kalousková, R.; Nevařil, D.; Prokopová, I. Blend of PVC and aliphatic-aromatic copolyesters on basis of recycled PET, Proceedings of the Polymery 2006, Třešť, Czech Republic, **2006**.
23. Brožek, J.; Žídková, M.; Malinová, L.; Kalousková, R. *J. Appl. Polym. Sci.* **2012**, *124*, 2395.
24. David, M.-O.; Prud'Homme, R. E. *J. Appl. Polym. Sci.* **1996**, *61*, 465.
25. Kalousková, R.; Markvart, L.; Kredatusová, J.; Brožek, J. *J. Appl. Polym. Sci.* **2009**, *114*, 826.