Polystyrene Modifications.   III.   Copolymers and Terpolymers of 2,5-Dichlorostyrene and 3,4-Dichlorostyrene*

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INTRODUCTION

The present work describes the copolymerization of various monomers with 2,5-dichlorostyrene and 3,4-dichlorostyrene.   Of particular interest are systems which are compatible and which exhibit improved craze resistance without sacrifice of thermal properties.

A code similar to that used in Part I[1] of this series will be used here to identify copolymers.   Thus, 2,5-ClS50A designates a 2,5-dichlorostyrene–acenaphthylene copolymer where the mole percentage of each monomer at initiation of polymerization is 50; 3,4-ClS50S refers to a copolymer of 3,4-dichlorostyrene–styrene prepared from equal moles of monomers.

Earlier reports[1,2] disclosed studies of styrene copolymers and substituted homopolymers in the amorphous unoriented state.   Although glass transition temperatures (T_g's) were increased by copolymerizing styrene with bulky monomers such as acenaphthylene, or by incorporation of methyl or chloro groups into the aromatic ring of polystyrene, such compositions crazed readily.   Incorporation of flexible side chains into styrene–acenaphthylene copolymers imparted flexibility to many systems, but did not result in improved craze resistance.

DISCUSSION

2,5-Dichlorostyrene was emulsion-polymerized to a high molecular weight polymer having a T_g of 110°C.   Polymerization under anhydrous conditions with $Al(C_2H_5)_3$–VCl_3 catalyst formed a low molecular weight amorphous polymer, and polymerization with $Al(C_2H_5)_3$–$TiCl_4$ catalyst gave a high molecular weight amorphous polymer.   Incorporation of relatively small amounts of acenaphthylene into emulsion polymerization systems produced modified poly(2,5-dichlorostyrenes) having high T_g's (Table I).

TABLE I
T_g's of Poly(2,5-Dichlorostyrene-co-Acenaphthylene)

Composition	$\{\eta\}$	T_g, °C.
2,5-ClS	0.63	110
2,5-ClS10A	0.92	141
2,5-ClS20A	0.56	155
2,5-ClS50A	0.74	147

Coating these copolymers from methyl ethyl ketone solution with the aid of a eoating knife produced dry films 4 mils thick which were more brittle than those of corresponding styrene copolymers.

Butadiene was incorporated into 2,5-dichlorostyrene–acenaphthylene copolymers in an effort to reduce brittleness, the butadiene being added 6 hrs. after initiation of polymerization. The properties of these terpolymers are summarized in Table II. Extrusions of these 2,5-ClSAB terpolymers gave brittle nonuniform inhomogeneous monofilaments. Before extrusion, the polymers were soluble; after, they were insoluble, indicating crosslinking had occurred.

TABLE II
Terpolymers of 2,5-Dichlorostyrene–Acenaphthylene–Butadiene[a]

Composition	T_g, °C.	Flexibility	Film clarity
2,5-ClS10A10B	83	Brittle	Clear
2,5-ClS20A10B	80	Very brittle	Clear
2,5-ClS10A15B	80	Flexible	Cloudy
2,5-ClS20A15B	61	Slightly flexible	Cloudy

[a] Butadiene was added to polymerization mixture 6 hrs. after initiation.

Poly(3,4-dichlorostyrene) was prepared by emulsion polymerization and cast into clear sheets having a glass transition temperature of 128°C., higher than that of poly(2,5-dichlorostyrene) (110°C.). Physical properties of an extruded monofil, extended 150% at 160°C., are listed in Table III.

3,4-Dichlorostyrene was copolymerized with monomers which would be expected to produce high T_g's. These copolymers (Table IV) appeared to

TABLE III
Physical Properties of Poly(3,4-Dichlorostyrene)

Polymer	$\{\eta\}$	Young's modulus $\times 10^{-4}$ kg./cm.^{2}	Tensile, kg./cm.^{2}	Elong., %	T_g, °C.
Koppers polystyrene (Atactic)	—	3.4	810	<4	100
Plax PB (sheet) polystyrene[a]	—	3.5	810	3.6–4.0	100
3,4-ClS	0.92	4.1	855	2.3	128

[a] Plax PB: Biaxially oriented polystyrene sheet.

TABLE IV
3,4-Dichlorostyrene Copolymers

Composition[a]	T_g, °C.	Film clarity
3,4-ClS50M$_n$	130	Hazy
3,4-ClS50N	130	—
3,4-ClS50S	121	Clear
3,4-ClS50S$_\alpha$	108	Hazy
3,4-ClS50Z	79	Slight haze
3,4-ClS50P$_m$	84	Slight haze
3,4-ClS25I$_m$	114	Slight haze
3,4-ClS25I$_b$	58	Slight haze
3,4-ClS25F$_E$	74	Slight haze
3,4-ClS25F$_b$	83	Slight haze
3,4-ClS50V$_c$	78	Hazy

[a] M$_n$ = methacrylonitrile, N = acrylonitrile, S = styrene, S$_\alpha$ = α-methylstyrene, Z = α-methylbenzyl methacrylate, P$_m$ = isopropyl methacrylate, I$_m$ = dimethyl itaconate, I$_b$ = dibutyl itaconate, F$_E$ = diethyl fumarate, F$_b$ = dibutyl fumarate, V$_c$ = vinylidene chloride.

be incompatible in the range studied, except for 3,4-ClS50S, which gave a clear film. All were brittle and crazed readily.

A second group of 3,4-dichlorostyrene copolymers was prepared of which the comonomers might be expected to impart greater flexibility to the chain (Table V). Except for the methyl acrylate and 2-ethylhexyl methacrylate and acrylate modifications, which were incompatible, these copolymers gave clear cast films. Imparting physical flexibility to cast sheets of modified poly(3,4-dichlorostyrene) did not, of itself, eliminate crazing. The methyl acrylate and n-butyl methacrylate modifications, though flexible, crazed severely under applied stress.

The compositions 3,4-ClS50H$_M$ and 3,4-ClS50H$_2$, both of which showed a reduced tendency to craze, were flexible and had low T_g's. In order to discover whether such craze resistance was due to unique structure or plasticization by residual solvent, both sheets were dried 96 hrs. at 55°C. in a vacuum oven. After drying, both sheets had lost 4.5% in weight

TABLE V
Incorporation of Acrylates and Methacrylates into Poly(3,4-dichlorostyrene)

Composition[a]	T_g, °C.	Film clarity	Flexibility	Crazing tendency
3,4-ClS50M$_a$	84	Slight haze	Flexible	Crazes
3,4-ClS50K	69	Clear	Slightly brittle	Crazes
3,4-ClS50H$_M$	59	Clear	Moderately flexible	Slight craze
3,4-ClS60K	49	Clear	Flexible	Crazes
3,4-ClS50X	46	Clear	Brittle	Crazes
3,4-ClS50H$_2$	41	Hazy	Flexible	Slight craze
3,4-ClS50E$_H$	43, 59	Hazy, waxy	Flexible	Blushes when creased

[a] M$_a$ = methyl acrylate, K = n-butyl methacrylate, H$_M$ = n-hexyl methacrylate, X = n-nonyl methacrylate, H$_2$ = 2-ethylhexyl methacrylate, E$_H$ = 2-ethylhexyl acrylate.
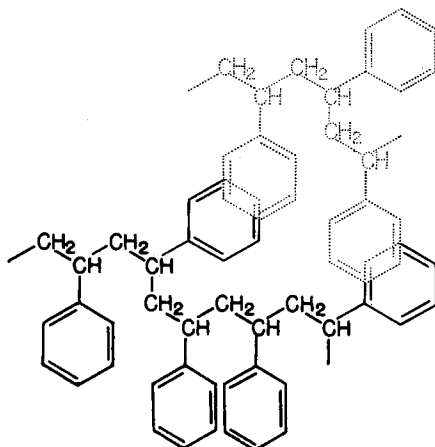
Fig. 1. Structure of unoriented Plax PB.

and were somewhat less flexible than before, but the resistance to crazing was unchanged. Of the two copolymers, 3,4-ClS50H$_M$ is of greater interest because, in contrast to 3,4-ClS50H$_2$, it is a compatible system. The hexyl methacrylate modification appeared to be unique in reducing crazing, since the corresponding n-butyl and n-nonyl ester copolymers showed no noticeable improvement in craze resistance.

Sheets of Plax PB, biaxially oriented polystyrene, 5 and 10 mils thick, showed much greater resistance to crazing than any unoriented modifications included in this paper. In order to form a sheet of unoriented polystyrene from Plax PB, the Plax was dissolved in benzene, coated, and dried to a sheet 8 mils thick. In contrast to oriented Plax PB, the unoriented sheet was extremely brittle and crazed readily. The high degree of crazing is related to physical entanglement of chains, the system being immobilized by bulky phenyl groups:

As noted in Part I, flexing of a polystyrene sheet caused crazing to appear on the side of the sheet exposed to tensile stress. In the unoriented system, tensile force is transmitted to entangled chains which cannot release the stress by slippage because of bulky phenyl groups. Although the theoretical tensile strength of a group of perfectly oriented chains would be extremely high (35–70 kg./mm.^{2} for polystyrene),[3] the actual tensile strength is much lower (about 8.1 kg./mm.^{2}), because applied stresses are distributed nonuniformly in less ordered systems. Applied stresses, then, are concentrated upon fewer chains in the entangled unoriented polystyrene system, and rupture occurs at C—C linkages not in the lowest potential energy state.

On studying the crazing tendencies of polystyrene, Högberg[4] stated that injection molding processes produced anisotropy which was caused by internal stress. Equalization of the stress occurred in the form of a tiny crack, the elongation at break being determined by the anisotropy.
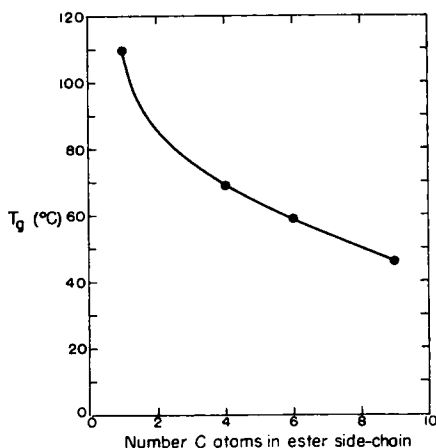
Fig. 2. T_g vs. ester side chain length in 50:50 3,4-dichlorostyrene–methacrylate ester copolymers.

Nielsen[5] demonstrated that, once bonds rupture in a polymer chain under applied tensile stress, forces set up within the zone of rupture are extremely high, causing other bonds in the region to rupture until the stress is relieved. Bond cleavage resulting in this manner forms minute cracks in the film which appear visually as craze marks.

Boundy and Boyer[6] have plotted the tensile strength against the degree of orientation of polystyrene. The higher tensile strength of more highly oriented samples indicates that tensile rupture of C—C bonds is involved in crazing, since more highly oriented samples craze least readily.

The correlation between bond rupture and crazing indicates that any release of stresses within the system by means other than bond rupture should eliminate crazing. Partial substitution of the bulky phenyl rings by smaller flexible groups should result in systems in which applied stress is relieved by slippage of chain segments rather than by breakage of C—C bonds. Obviously, in order to retain desirable thermal and physical properties of polystyrene, the percentage of flexibilizing modifier in the molecule should be as low as possible.

The loss in T_g encountered in designing more flexible polystyrene systems was minimized by basing the copolymers on poly(3,4-dichlorostyrene) ($T_g = 128°C.$). Any increase in physical bulk of side chains due to ring substitution of chlorine atoms does not seem to be important in its effects on crazing, since unoriented polystyrene and unoriented poly(3,4-dichlorostyrene) craze to the same extent. A comparison of tensile strengths of oriented 3,4-ClS with oriented polystyrenes (Table III) also indicates that chain rupture is approximately the same in both compositions. Possibly the phenyl ring is sufficiently large to exert a maximum effect in preventing chain slippage; any further increase of ring size through substitution would cause no increase in entanglement with other chains.
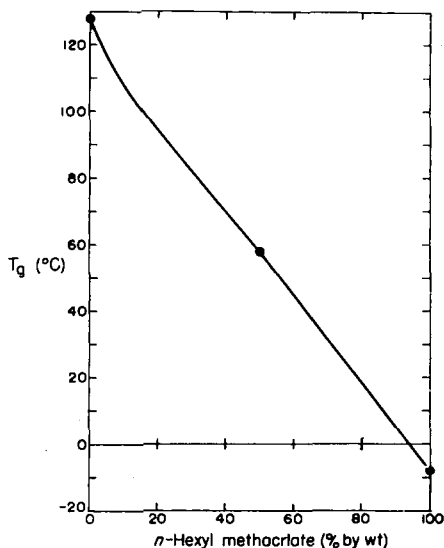
Fig. 3. Variation of T_g with n-hexyl methacrylate content in 3,4-SH$_M$ copolymers.

The reduction of T_g produced by incorporation of various linear methacrylate esters into poly(3,4-dichlorostyrene) is outlined in Figure 2. Higher methacrylate esters cause greater reduction in T_g.

Since T_g's of 3,4-ClS homopolymer, 3,4-ClS50H$_M$, and poly(n-hexyl methacrylate) are known, the T_g's of other 3,4-ClSH$_M$ copolymers can be estimated (Fig. 3). From the curve it can be seen that the copolymer having 15 mole-% hexyl methacrylate should give a T_g equal to 100°C., that of polystyrene homopolymer. Transition measurements of these copolymers in this range by differential thermal analysis (DTA) are not sharp, however; 3,4-ClS20H$_M$ appears to soften in the range 50–100°C. with no sharp transitions. The DTA curve appears to be one that would be observed if small blocks of varying 3,4-dichlorostyrene/n-hexyl methacrylate ratios were present. The different blocks would show small transitions at various points, but the concentration of blocks of any one copolymer ratio would be too small to produce a well-defined peak.

As noted earlier, the addition of a flexibilizing component to a polystyrene or substituted polystyrene system is not, in itself, sufficient to reduce crazing. The copolymer must attain a uniqueness of structure that will allow internal chain movement under applied stress. A schematic drawing of a poly(3,4-dichlorostyrene-co-methacrylate ester) is shown in Figure 4. Shorter side chains such as structure III impart flexibility to each chain by allowing freedom of movement at certain points along a given chain. However, the short side chains cannot prevent aromatic rings of adjacent chains from interlocking to immobilize the system. When side chains become longer, however, they act as barriers between phenyl rings from adjacent chains, preventing them from interlocking (structure III).
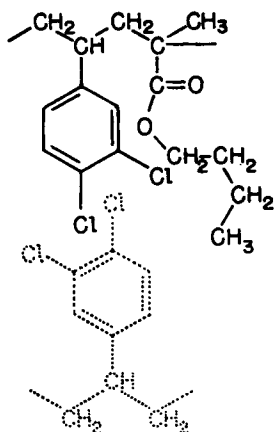
(a)
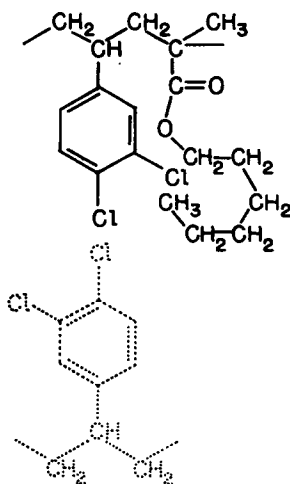
(b)

Fig. 4. Structure of (a) Poly(3,4-dichlorostyrene-co-n-butyl methacrylate) and (b) Poly(3,4-dichlorostyrene-co-n-hexyl methacrylate).

Since stresses can now be released by movement of adjacent chain segments in the vicinity of hexyl methacrylate segments, bond rupture will occur less frequently and only upon imposition of higher stresses.

In considering the poly(3,4-dichlorostyrene-co-methacrylate ester) systems, it might reasonably be assumed, since the 3,4-ClS50H$_M$ composition shows improved resistance to crazing, that substitution of higher methacrylate esters would accomplish the same result. Higher ester com-
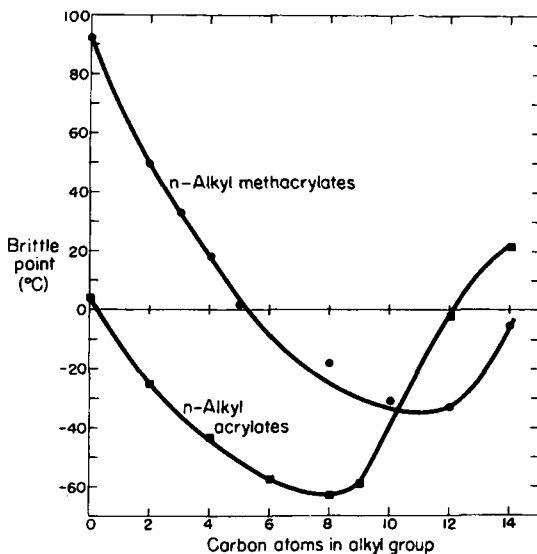
Fig. 5. Brittle points of polymeric n-alkyl acrylates and methacrylates.

positions, such as 3,4-ClS50X, craze readily, however (Table V). Rehberg and Fisher[7] have noted that higher poly(alkyl acrylates and methacrylates) form crystalline waxes. By plotting the brittle points of the poly-(n-alkyl acrylates and methacrylates) against the number of carbon atoms in the alkyl group, they obtained curves in which brittle points decreased to a minimum and then increased at longer chain lengths (Fig. 5). The brittle point of n-alkyl methacrylates reached a minimum at 11 carbon atoms, and that of the n-alkyl acrylates at 8. The increasing brittle points at longer side chain lengths define the systems as being immobilized through side chain crystallization. At side chain lengths somewhat shorter than those at which brittle points begin to increase, some crystallinity is undoubtedly present. The extent of crystallinity in the lower poly(n-alkyl methacrylates) is too small to overcome the larger transition of the randomly arranged chain backbone and is, therefore, not observed in brittle point measurements.

The absence of side chain crystallization explains the uniqueness of the poly(3,4-dichlorostyrene-co-n-hexyl methacrylate) composition in exhibiting improved craze resistance. The alkyl side chain of the hexyl ester is sufficiently long and mobile to permit internal movement under stress by separating phenyl rings of different chains; it is not sufficiently long, however, to crystallize. The crystallization occurring in longer side chains again forms a system unable to adjust to imposed forces without bond cleavage.

The improved craze resistance of 3,4-ClS50H$_M$ was obtained at the expense of reduced T_g (59°C., as compared with T_g = 128°C. for 3,4-ClS). In order to observe crazing tendencies in a 3,4-ClSH$_M$ system of low H$_M$

content, a 3,4-ClS20H$_M$ was prepared and coated to produce a sheet. Although the crazing appeared more readily in 3,4-ClS20H$_M$ than in 3,4-ClS50H$_M$, it was not as severe as that of unoriented polystyrene or unoriented 3,4-ClS. Since orientation of polystyrene has been shown to increase craze resistance, it seems evident that poly(3,4-dichlorostyrene-co-n-hexyl methacrylate) would also be improved by this procedure.

EXPERIMENTAL

Monomers

Liquid monomers were distilled and stored in a freezer at −20°C. Solid monomers were generally used as received from the manufacturer and were also stored at −20°C. Acenaphthylene obtained from the Aldrich Chemical Company was recrystallized from methanol to give glistening yellow plates, m.p. 89–90°C. (uncorr.).

Polymerizations

A. Emulsion Polymerization of 2,5-Dichlorostyrene–Acenaphthylene–Butadiene

Monomer mixture, 20 g., 1 drop of dodecanethiol, and 6 drops of cumene hydroperoxide were added to a solution of 4 mg. of ferric sulfate, 100 mg. of fructose, 30 mg. of sodium pyrophosphate decahydrate, and 1.0 g. of N-oleyl-N-methyltauramide in 30 ml. of distilled water. Butadiene was added in slight excess, and the tared 4-oz. pressure bottle was allowed to reach correct weight by evaporation of butadiene. After capping, the bottle was tumbled in a water bath at 40°C. for 16 hrs. The emulsion was poured into a half-pint freezer carton and frozen at −20°C. After thawing, the solid was filtered, washed thoroughly with water, washed with methanol, and dried in a vacuum oven at 30°C.

Terpolymers of 2,5-dichlorostyrene–acenaphthylene–isoprene were made by the same procedure.

B. Emulsion Polymerization

The following system was used for polymerization of monomers not mentioned in Section A. A 10 g. quantity of monomer mixture was placed in a 4 oz. pressure bottle, and 24 moles of distilled water, 0.4 g. of N-oleyl-N-methyltauramide, 0.1 g. of potassium metabisulfite, and 0.2 g. of potassium persulfate were added. The bottle was flushed with nitrogen, capped, and tumbled in a 30°C. water bath for 44 hrs. At the end of this time samples containing more than 10% acenaphthylene were incompletely polymerized and were tumbled an additional 96 hrs. at 40°C. Samples were purified as described in Section A.

Coating of Sheets

A 1-g. portion of polymer was dissolved in 9 g. of methyl ethyl ketone and spread on a glass plate by means of a coating knife. The film was air-dried for 48 hrs. Samples having improved flexibility or craze resistance were further dried in a vacuum oven at 55°C. for 96 hrs. Dried films were 4 mils thick.

Measurement of Crazing

A cast sheet of polymer 4 mils thick and 1 in. long was placed between the jaws of a small vise. By slowly closing the jaws of the vise, the film was bent. The point at which crazing first occurred was determined visually; at this point, the distance between the jaws of the vise was measured. The smaller this distance, the greater was the degree of craze resistance of the cast sheet.

Measurement of T_g

Softening points were determined by placing the sample in a standard metal melting-point block and passing a beam of light through the apparatus. The intensity of the beam was measured by a light intensity indicator.

Samples were placed off-center so as to be out of the main light beam. A metal cover with a small hole in the center was placed over the sample at an angle, thus blocking off part of the main light beam from the intensity recorder. At the softening point, plastic flow of the sample caused the cover to become more nearly horizontal, thus increasing the amount of light passing through the hole in the cover. To determine softening points below room temperature, the apparatus was cooled with dry ice.

This procedure gave softening points which were in close agreement with T_g's determined by DTA except in those examples where polymers were crystalline. For this reason, values in this paper have been listed as T_g's rather than as softening points.

CONCLUSIONS

Copolymers based on 2,5-dichlorostyrene appeared to offer little improvement over polystyrene in craze resistance or in T_g. The high T_g and the physical properties of poly(3,4-dichlorostyrene) made it attractive as a basic composition for modification. Although most of the 3,4-ClS copolymers studied were brittle and crazed badly, two copolymer systems exhibited reduced crazing, 3,4-ClS50H$_2$ and 3,4-ClSH$_M$. The ethylhexyl methacrylate copolymer was incompatible; the n-hexyl methacrylate–3,4-dichlorostyrene copolymer was a compatible system and was unique among n-alkyl methacrylates in showing reduced tendency to craze. Crazing was shown to be a characteristic of entangled immobile chain systems and could be reduced by biaxial orientation.

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Synopsis

Thermal properties and resistance to crazing of copolymers and terpolymers of 2,5-dichlorostyrene and 3,4-dichlorostyrene have been studied. Copolymers based on 2,5-dichlorostyrene showed little or no improvement over polystyrene in craze resistance or glass transition temperature. Although copolymers of 3,4-dichlorostyrene were generally brittle and crazed readily, poly(3,4-dichlorostyrene-co-2-ethylhexyl methacrylate) and poly(3,4-dichlorostyrene-co-n-hexyl methacrylate) crazed less readily than polystyrene.

Résumé

On a étudié les propriétés thermiques et la résistance au craquelage de polymères ternaires de 2,5-dichlorostyrène et de 3,4-dichlorostyrène. Les copolyméres à base de 2,5-dichlorostyrène ne montrent presque pas d'avantage sur le polystyrène quant à la température de transition à l'état vitreux, ou quant à la résistance au craquelage. Les copolyméres de 3,4-dichlorostyrène étaient généralement fragiles et facilement craquelés, excepté le poly(3,4-dichlorostyrène-co-2-éthylhexyl méthacrylate). Ceux-ci se craquèlent moins facilement que le polystyrène.

Zusammenfassung

Thermische Eigenschaften sowie Rissbeständigkeit von Copolymeren und Terpolymeren mit 2,5-Dichlorstyrol und 3,4-Dichlorstyrol wurden untersucht. Copolymere mit 2,5-Dichlorstyrol zeigten nur geringe oder keine Verbesserung der Rissfestigkeit oder Glasumwandlungstemperatur gegen Polystyrol. Obgleich Copolymere mit 3,4-Dichlorstyrol im allgemeinen spröde waren und zur Rissbildung neigten, zeigten doch Poly-(3,4-dichlorstyrol-co-2-äthylhexylmethacrylat) und Poly-(3,4-dichlorstyrol-co-n-hexylmethacrylat) eine geringere Tendenz zur Rissbildung als Polystyrol.