# Polymer additive analysis by pyrolysis–gas chromatography
# I. Plasticizers

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## Abstract

Plasticizers are widely used in thermoplastic polymers to modify their physical properties and processibility. Plasticizers as well as most of the other additives in the polymer can be qualitatively analyzed by pyrolysis–gas chromatography (Py–GC) simultaneously with the polymer composition. The key to the successful analysis of plasticizers not only requires a comprehensive understanding of commercial plasticizers but also requires knowledge of the polymer and its applications, as well as the Py–GC technique. In this study, several plasticizers in different polymeric systems were studied to demonstrate the utility of Py–GC as a good tool for the characterization of these systems. The advantages of using Py–GC for plasticizer analysis are also discussed. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

A plasticizer is defined by the International Union of Pure and Applied Chemistry (IUPAC) as a substance or material incorporated in a material (usually a plastic or an elastomer) to increase its flexibility, workability or extensibility. A plasticizer may reduce the melt viscosity, lower the temperature of a second-order transition or lower the elastic modulus of the product. Most plasticizers are liquids of low volatility. In many circumstances, they are blended to produce a wide range of physical properties from a single parent polymer.

The critical considerations for selection of a plasticizer for the modification of the properties of a polymeric system are compatibility, permanence, aging and its effects on the other properties [1]. A plasticizer must be capable of being mixed uniformly and homogeneously and remain blended when cooled to room temperature and throughout the useful life of the plastic product. The stability of the plasticizer in its mixed state must be maintained during the useful life of the product. A plasticizer may migrate from the material to cause impermanence because of volatility, exudation, extraction or other influences in the application environment. It may degrade by chemical, radiation, or other conditions that exist in the application surroundings. A plasticizer may affect other physical properties of the polymer such as adhesion, electrical properties, flammability and toxicity. The choice of plasticizer must consider its efficiency for modification of the desired properties, as well as optimization of its effect on other properties.

There are several major theories have been proposed to explain the mechanism of plasticization. There are the lubricity theory, the gel theory and the free volume theory. The lubricity theory is based on

the fact that since the major force resisting deformation of a polymer is intermolecular friction, the plasticizer would act as a lubricant, separating the polymer chains and facilitating their movement over each other. The gel theory depended on the fact that since the intermolecular force resulted from those ''points of interaction'' such as dipole–dipole interaction or hydrogen bonding, when plasticizer solvates the polymer, it destroys many of these ''points of interaction'' by replacing polymer–polymer interactions with polymer–plasticizer interaction. The free volume theory originated from consideration of the nature of the glass transition in super-cooled liquids and amorphous polymers. Plasticizers are much smaller molecules and have much greater free volume. The addition of plasticizer has the effect of increasing the free volume of the plasticized polymer that let the movement of the polymer chain easier.

Because the role and purpose of a plasticizer in a polymer system are well defined, it is easy to understand which polymeric systems often utilize plasticizers to modify their physical properties to match the applications' needs. Polyvinyl chloride (PVC) and its copolymers [2] are the most important polymers that rely on plasticizers to extend their physical properties to fulfill a board range of applications. Cellulose derivatives [3] depend on plasticizers to bring the processing temperature (melt flow temperature) down below the polymer decomposition temperature. Other thermoplastic polymers may add specific types of plasticizers for a well-defined application. However, their magnitude of dependence on plasticizer level is much reduced relative to the two polymeric systems mentioned above.

There are many ways to classify plasticizers. They may be categorized by molecular mass, molecular structure, compatibility, cost efficiency or purpose of application. From an analytical point of view, plasticizers may be classified by their molecular structure [4] because the molecular structure is directly related to polarity and molecular flexibility, which will affect their properties. Based on the molecular structure, plasticizers can be divided into several major groups [5]: (1) phthalic acid esters; di(2-ethylhexyl) phthalate (DOP), butyl benzyl phthalate (BBP) and dibutyl phthalate (DBP) are several important examples; (2) phosphoric acid esters; trioctyl phosphate (TOP), diphenyl 2-ethylhexyl phosphate and tri(2-ethylhexyl) phosphate are typical compounds used; (3) polyfunctional fatty acid esters; butyl and octyl adipate, sebacate, citrate and maleates are commonly used plasticizers; (4) polymeric plasticizers; polymeric plasticizers are oligomers or polymers of molecular mass above 500 used for plasticizers. They include polyglycols, polyesters, polyepoxides and chlorinated polyolefins.

The most common way to incorporate plasticizers into polymers is by blending, that is, by physically mixing with the polymer molecules. When analyzing the plasticizers, it is relatively straightforward to separate them just by solvent extraction. After separating the plasticizer from the polymer, the plasticizer-containing portion can be further separated/analyzed by proper chromatographic methods with the appropriate detection [6,7]. Because these procedures involve a series of wet-chemistry steps as well as chromatographic procedures, it is a time and labor intensive operation. However, some polymers are insoluble in most solvents, such as the nylon family. Although there may be a solvent that can dissolve them, the conditions required are often at high temperatures or the viscosity of final solution is so high that the extraction is practically impossible or the solvent is very corrosive and presents safety hazards.

Pyrolysis–gas chromatography (Py–GC) [8] is an important technique for polymer analysis. Py–GC is a technique that uses thermal energy (pyrolysis) to break down a polymeric chain to monomers, oligomers and other fragments, followed by the separation of the pyrolysates with GC and detection with appropriate detectors. Flame ionization detection (FID) is one of the most frequently used detection methods for quantitative analysis of pyrolysates. Mass spectrometry (MS) or mass-selective detection is one of the most commonly used detection methods for identification. The intensities of monomers or monomer-related fragments are commonly used to obtain compositional data [9]. The oligomers or oligomer-related fragments are used to elucidate microstructure as well as composition information [10].

Plasticizers, as well as most other additives in the polymer, can be qualitatively and quantitatively analyzed by Py–GC simultaneously with the polymer composition and microstructure. The key to the

successful analysis of plasticizers not only requires a comprehensive understanding of commercial plasticizers but also requires knowledge of the polymer and its applications, as well as the Py–GC technique. In this study, several plasticizers in different polymeric systems were studied to demonstrate the utilities of Py–GC as a good tool for the characterization of these systems. The advantages of using Py–GC for plasticizer analysis are also discussed.

## 2. Experimental

### 2.1. Polymers

PVC flexible tubing (Tygon tubing) was made by Norton Performance Plastic (Arkon, OH, USA) and was purchased from Fisher Scientific (Pittsburgh, PA, USA). A cellulose propionate polymer (catalog No. 45,490-7) was purchased from Aldrich (Milwaukee, WI, USA). A vinyl chloride–vinylidene chloride copolymer film was obtained from Asahi (Tokyo, Japan). An impact-modified polystyrene blended with polycarbonate (PC-HIPS) polymer, grade Daicel X7200L, was obtained from Daicel (Tokyo, Japan). A polyurethane adhesive/sealant was obtained from Sika (Madison Heights, MI, USA). The butadiene–acrylonitrile copolymer (catalog No. 530) and PVC (catalog No. 355) were purchased from Scientific Polymer Products (Ontario, NY, USA). The styrene–butyl acrylate copolymer was synthesized in the laboratory with a textbook method [11]. The butadiene–acrylonitrile copolymer and PVC blend polymer were made in the laboratory. All polymers purchased were used as received without any further purification.

### 2.2. Py–GC conditions

Samples of polymer (approximately 0.5 mg) were carefully deposited into a quartz tube. The quartz tube was inserted in a 300°C interface connected to the injection port of a Hewlett-Packard (HP) Model 6890 gas chromatograph equipped with a FID system. The samples were pyrolyzed (CDS 2000 Pyroprobe, Pt coil) at a calibrated temperature of 700°C. The coil was heated to the calibrated temperature at 20°C/ms and held at the set temperature for a 20-s

interval. The pyrolysis products were split in the 300°C injection port, with 250:1 split ratio. The GC system was set up with a fast-flow program (15 p.s.i./0.2 min, 75 p.s.i./min, to 90 p.s.i./8.8 min) (1 p.s.i.=6894.46 Pa). The separation was carried out on a fused-silica capillary column (J & W Scientific DB-5, 10 m×0.10 mm I.D., 0.4 μm film) using a fast-temperature ramping program (50°C/0.2 min, 100°C/min, to 100°C/0 min; 80°C/min, to 140°C/0 min; 60°C/min, to 200°C/0 min; 50°C/min, to 280°C/0 min; 40°C/min, to 320°C/5.2 min).

### 2.3. Py–GC–MS conditions

The sample preparation and pyrolysis in the Py–GC–MS experiments were the same as the for the Py–GC experiments. The GC used was a HP Model 5890 gas chromatograph. The pyrolysis products were split in the 300°C injection port, with 10 p.s.i. head pressure, and 30:1 split ratio. The pyrolysis products were separated on a fused-silica capillary column (J & W Scientific DB-5, 30 m×0.25 mm I.D., 1.0 μm film) using a linear temperature program (40°C/4 min, 10°C/min, to 320°C/18 min) and detected by a HP 5791 mass-selective detector. The GC output region to the mass-selective detector was kept at 300°C. An electron ionization mass spectrum was obtained every second over the molecular mass range of 15 to 650. The results of Py–GC–MS were used mainly for component identification.

### 2.4. Evolved gas analysis conditions

A sample of polymer (approximately 0.5 mg) was deposited into a Pt cup and loaded on top of a micro-oven type pyrolyzer (Frontier Lab., Model Py-2010D). The pyrolyzer is operated in the evolved gas analysis mode. The pyrolyzer is directly connected to the injection port of a Hewlett-Packard (HP) Model 5890 gas chromatograph equipped with a FID system. The micro-oven is temperature programmed at 100°C/5 min, 20°C/min, to 700°C/5 min. The evolved gas products were split in the 300°C injection port, with 15 p.s.i. head pressure, and 30:1 split ratio. The evolved gas products flowed directly through a deactivated fused-silica capillary column (approximately 50 cm) which was directly connected from injection port to the detector. The

GC oven was kept at 300°C, and the detector was also kept at 300°C.

## 3. Results and discussion

Fig. 1 shows a pyrogram of flexible PVC tubing (Tygon tubing) which is commonly used in the chemical laboratory for water and gas lines. All major peaks labeled in the figure have been identified and listed in the figure's caption. The plasticizer used in this tubing material is di(2-ethylhexyl) phthalate. The mass spectrum is shown in Fig. 2. In non-food related flexible PVC applications, the family of alkyl substituted phthalate esters has been widely used. However, the identification of those alkyl-substituted phthalate esters through their electron ionization mass spectra is not as simple as a library search and match, because the mass spectra for this phthalate

ester family are all very similar. One reason for the similarity is most phthalate esters do not give an intense parent ion in their mass spectra. In addition, all phthalate esters have common major fragments. As shown in Fig. 2, the major ions such as $m/z$ 167 and 149 correspond to phthalate acid and phthalate anhydride. The key to identifying them has to depend on the minor fragments (for example ion mass 279 in this case) as well as the retention time through GC separation.

Most cellulose and its derivative polymers are highly polar and have little chain flexibility. In addition, they have rigid ring structures in the backbone. Thus, it is necessary to plasticize them to improve melt processibility and impact resistance in order to provide some flexibility in film and sheet applications. Fig. 3 shows a pyrogram of cellulose propionate with a dioctyl adipate plasticizer. Under Py–GC conditions, the cellulose backbone does not
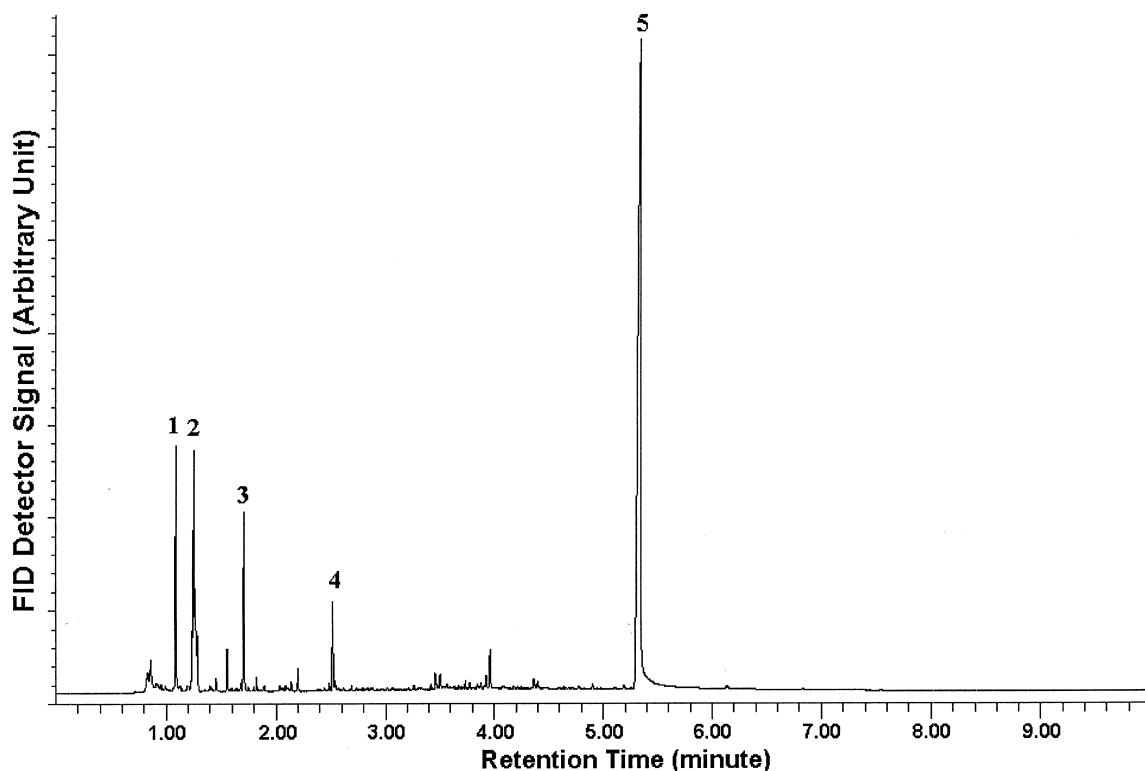


Fig. 1. The pyrogram of PVC tubing (Tygon tubing) with di(2-ethylhexyloctyl) phthalate as plasticizer. The identification of major pyrolysates is (1) benzene, (2) octene isomers, (3) 2-ethylhexyl aldehyde isomers, (4) 2-ethylhexyl alcohol isomers, (5) di(2-ethylhexyl) phthalate.
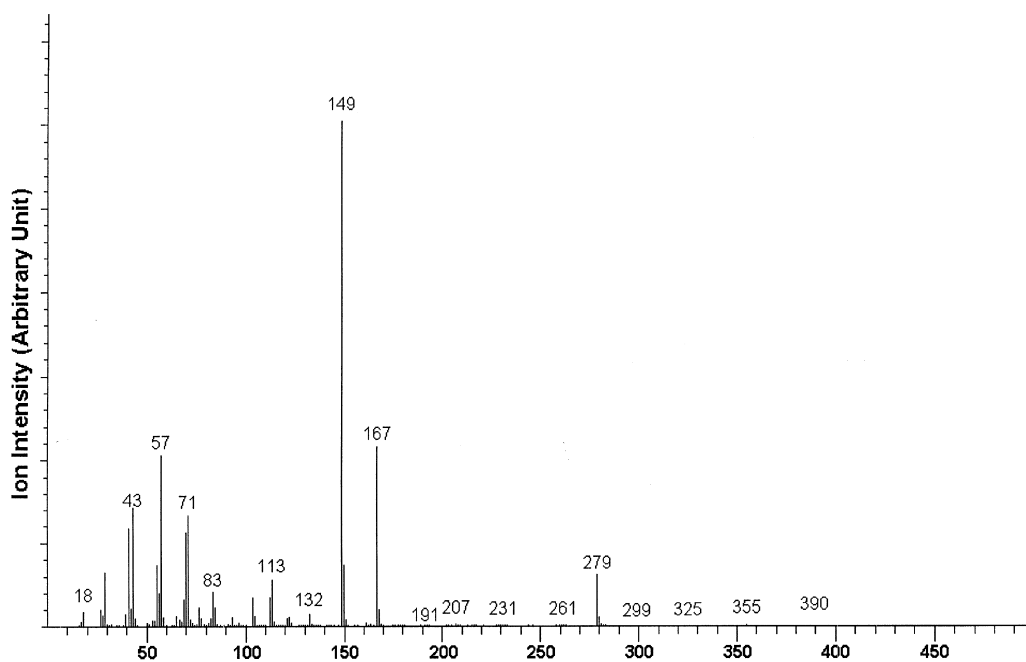
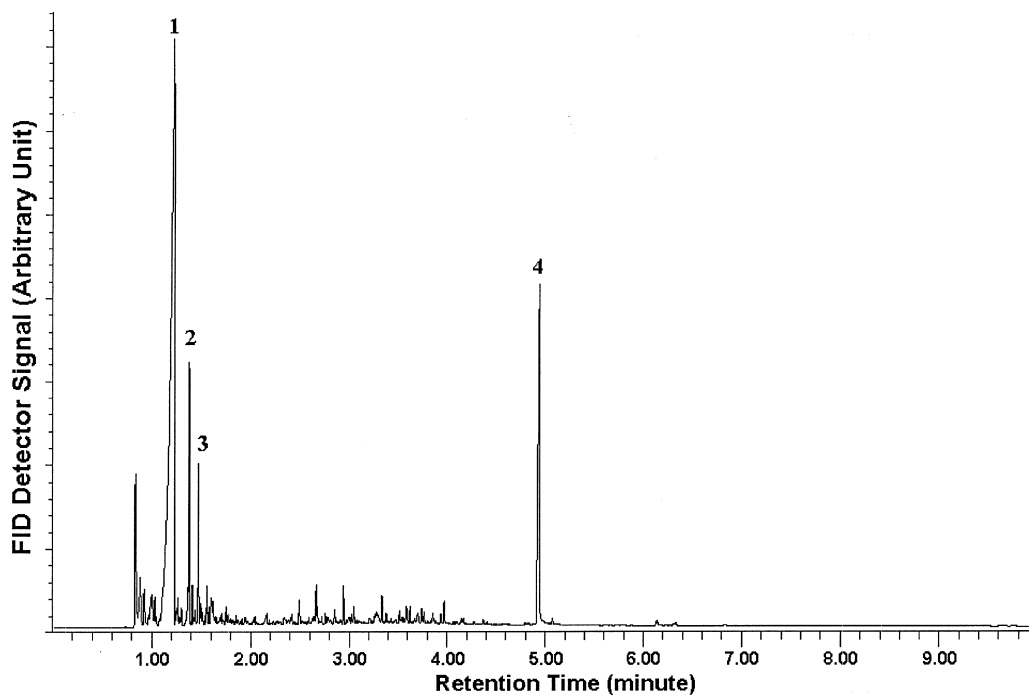Fig. 2. The mass spectrum of di(2-ethylhexyl) phthalate.



Fig. 3. The pyrogram of cellulose propionate with dioctyl adipate as plasticizer. The identification of major pyrolysates is (1) propanoic acid, (2) acetyl propanonate, (3) propanoyl propanonate, (4) dioctyl adipate.

produce any major pyrolysates, instead, the propanoic derivatives show several important fragments. The plasticizer, dioctyl adipate, is present as a clearly volatized component in the pyrogram.

Plasticizers have been used in many polymers for different applications where flexible properties are needed. However, certain types of applications may have some special requirements such as polymer films used in food/meat packaging that require storage at low temperatures for a period of time. Fig. 4 shows a pyrogram of a vinyl chloride–vinylidene chloride copolymer film. All major peaks labeled in the figure have been identified and listed in the figure's caption. The major application of this copolymer is a film that is used for food packaging. The plasticizer used in this case is a mixture of dibutyl sebacate and tributyl acetylcitrate. The use of alkyl substituted aliphatic esters instead of the alkyl substituted phthalate esters as a plasticizer in this

case may be to improve low temperature properties to fulfill this food/meat packaging application requirement where refrigeration is frequently necessary.

There are many cases where more than one plasticizer is used to plasticize a polymer system. For example, in the film of vinyl chloride–vinylidene chloride copolymer, two types of plasticizers (dibutyl sebacate and tributyl acetylcitrate) were used. One of them serves as the primary plasticizer and the other as secondary plasticizer. They are many reasons to use two plasticizers. One of them may not be completely miscible with the polymer at the desired level, certain physical properties cannot be obtained by just one plasticizer, or it may be more cost effective to use two plasticizers, etc.

The plasticizer used in the polymer does not have to be a pure compound as long as it performs the plasticizing function in the polymer. Depending on
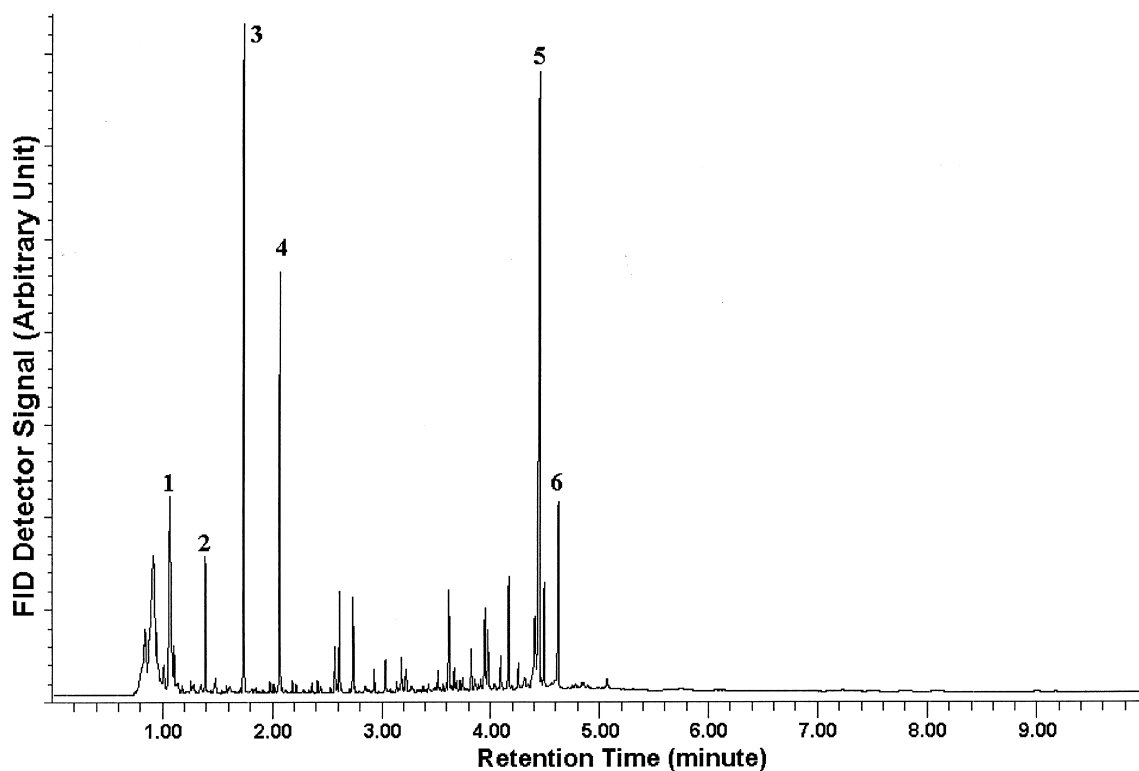


Fig. 4. The pyrogram of vinyl chloride–vinylidene chloride copolymer film with a mixture of different plasticizers. The identification of major pyrolysates is (1) benzene, (2) chlorobenzene, (3) dichlorobenzene, (4) triichlorobenzene, (5) dibutyl sebacate, (6) tributyl acetylcitrate.

its origin, it can be a mixture of isomers. For economic purposes, this mixture may not be purified or separated. Fig. 5 shows a pyrogram of a polyurethane sealant with plasticizer. The plasticizer used in this case is a mixture of didecyl phthalate esters. The presence of an alkene mixture, alkyl alcohol mixture, and the broad peak of phthalate ester mixture in the pyrogram provide the evidence that this plasticizer is a mixture. The use of a mixture as a plasticizer is different from the primary and secondary plasticizers discussed previously. The use of a mixture as a plasticizer is usually for economic reasons alone.

There are no definite dividing lines among the polymer additives of various types. Plasticizers may serve another function such as lubricant, processing aid, impact modifier, thermal stabilizers, or flame retardant. Fig. 6 shows a pyrogram of an impact-modified polystyrene–polycarbonate blend. The

plasticizer used in this polymer is triphenyl phosphate (TPP). TPP not only serves as a plasticizer in this case, but also serves as a flame retardant.

Owing to the fact that most plasticizers are incorporated into a polymeric system through blending, they can easily be separated by solvent extraction. However, they may also be separated and detected by a thermal method. Fig. 7 shows an evolved gas analysis (EGA) experimental plot (signal intensity versus temperature) from 100°C to 700°C for an impact-modified polystyrene and polycarbonate blend. During the temperature ramping from 100°C to 700°C, the TPP is the first material evolved. TPP is evolved starting at 170°C and is finished at approximately 330°C. The rest of the polymer, because the impact-modified polystyrene and polycarbonate are blended, may be evolved separately depending on their decomposition temperature. The impact-modified polystyrene is evolved approximate-
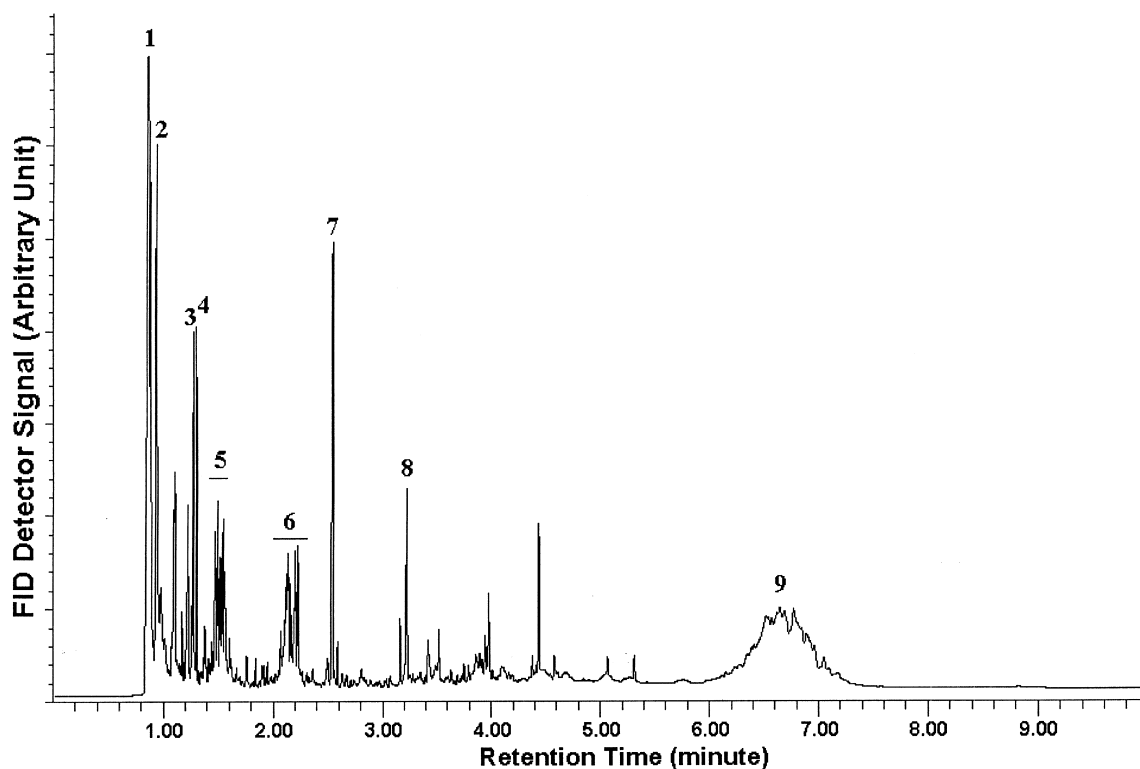


Fig. 5. The pyrogram of polyurethane sealant with a plasticizer mixture. The identification of major pyrolysates is (1) propene, (2) propanol, (3) diisopropyl ether, (4) 1-(1-methylethyloxy)-2-propanone, (5) decene isomers, (6) decanal isomers, (7) phthalic anhydride, (8) isophorone diisocyanate, (9) didecyl phthalate isomers.
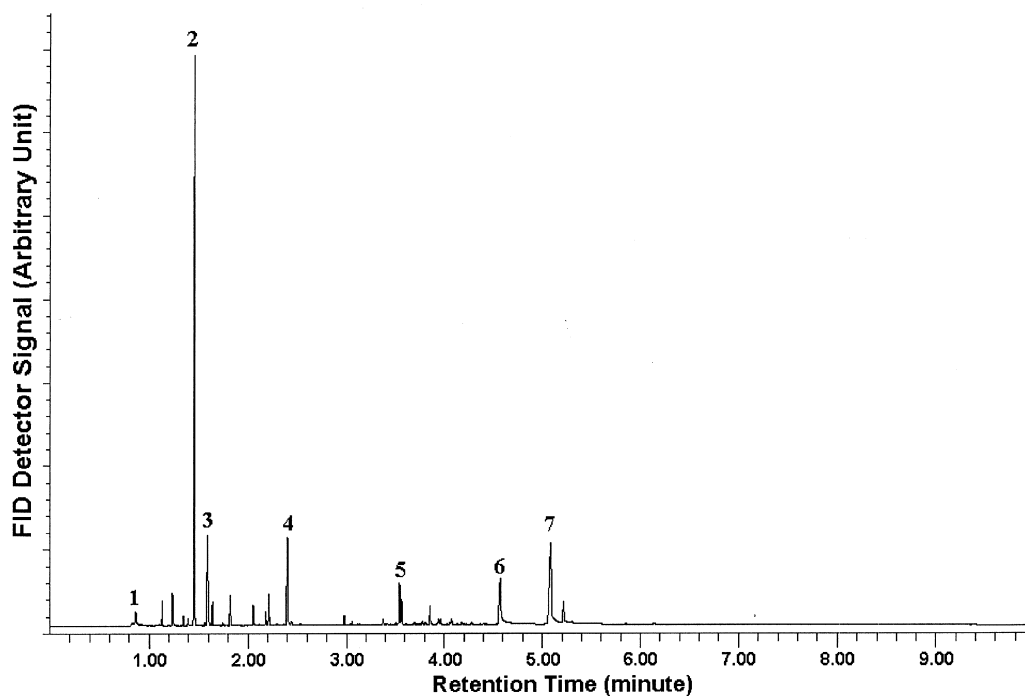
Fig. 6. The pyrogram of impact-modified polystyrene–polycarbonate resin with a dual-purpose plasticizer. The identification of major pyrolysates is (1) butadiene, (2) styrene, (3) phenol, (4) ethylmethyl phenol, (5) styrene dimer, (6) bisphenol A, (7) triphenyl phosphate.
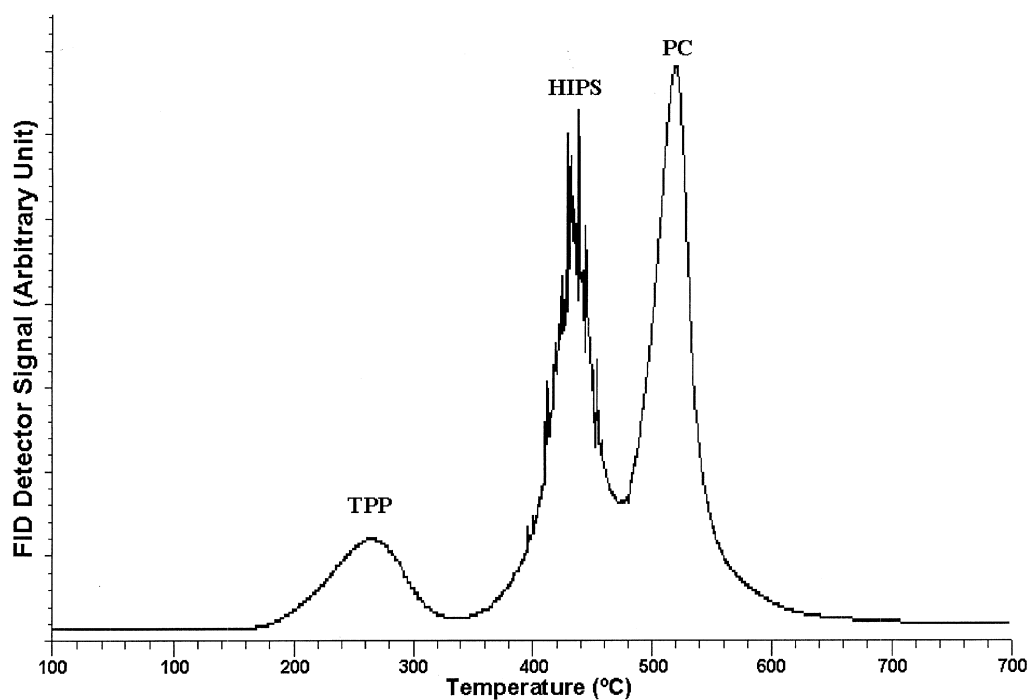


Fig. 7. An evolved gas analysis experimental plot (signal intensity versus temperature) from 100°C to 700°C for impact-modified polystyrene and polycarbonate blend polymer.

ly between 350°C and 540°C and the polycarbonate is evolved from approximately 440°C to 710°C. The speed of micro-oven temperature ramping has a critical effect on the broadening of the peak. The other reasons for the peak broadening for impact-modified polystyrene and polycarbonate may be the kinetic factors or the molecular mass distribution of each polymer. Because they are polymers, each polymeric molecule is not exactly the same (from a molecular mass point of view). They contain a distribution of repeat monomer units in the polymeric molecules with different chain lengths (or different molecular masses). The reason for the sharp spikes in the impact-modified polystyrene is not clear. It may be the result of different sizes of polybutadiene phases in the polystyrene.

Based on the EGA result, if one pyrolyzed this polymer at 350°C, TPP may be separated out from this polymer system. Fig. 8 shows the result of a stepwise pyrolysis experiment. The first pyrogram shows the polymer pyrolyzed at 375°C, and the second pyrogram is the consecutive pyrolysis of the same polymer at 700°C. It is quite clear that both impact-modified polystyrene and polycarbonate will not decompose at 375°C [12,13]. In the 375°C pyrogram, only TPP is observed. This seems to be a very effective extraction method (it may be called ''temperature extraction'' or ''thermal desorption'') which only extracts the TPP from this polymer system.

One of the major concerns when plasticizers are added to the polymer is the volatility of plasticizers because the main cause of impermanence is the volatility of plasticizers. One way to improve this problem is to use the polymeric types of plasticizers. Polymeric types of plasticizers may be blended into the polymers, grafted onto the polymer molecules, or copolymerized with other monomers into polymer. There are two major ways of incorporating polymeric plasticizers. The first way is blending or
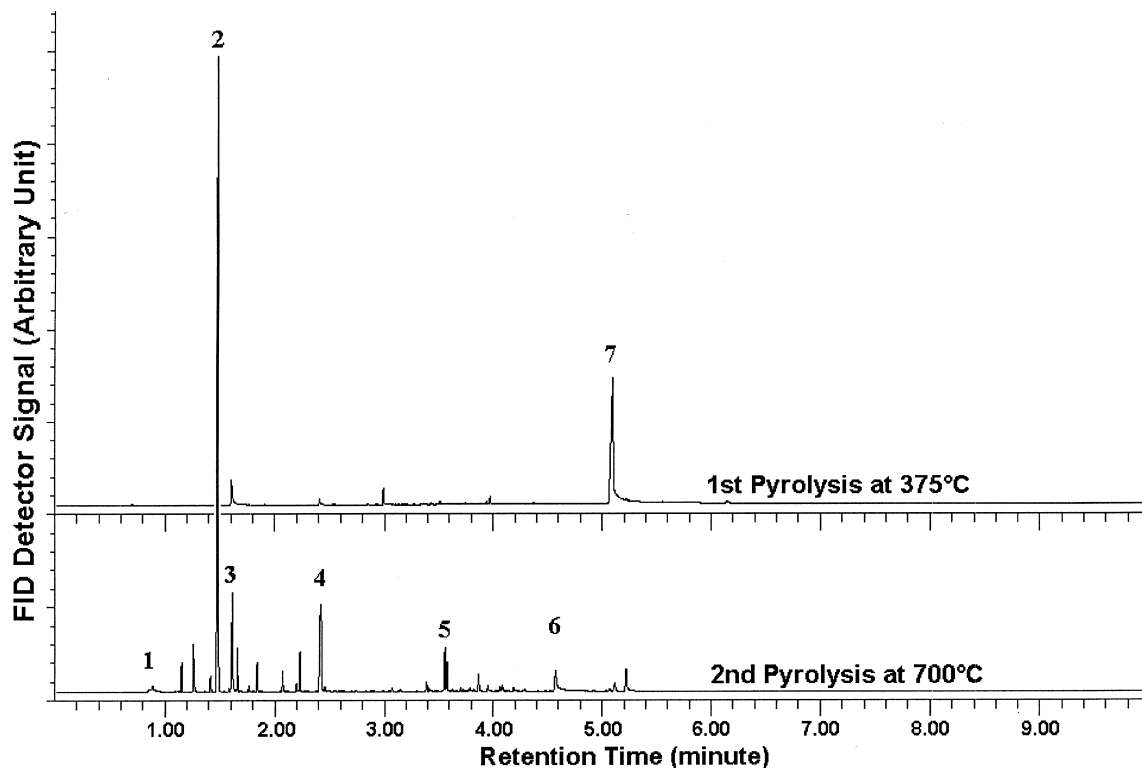


Fig. 8. The pyrogram of stepwise pyrolysis for impact-modified polystyrene–polycarbonate resin. The first pyrolysis at 375°C followed by the second pyrolysis at 700°C.

grafting the polymer with polymeric plasticizers to attain the desired property. The polymeric plasticizers produce good flexibility and offer the ultimate in permanence. One example of this case is the butadiene–acrylonitrile copolymer (nitrile rubber)

used as a plasticizer for PVC. The advantages of nitrile rubber addition to PVC have been discussed in several applications [14,15]. Essentially, it offers better low temperature flexibility and a wider service temperature range. Fig. 9 shows pyrograms of nitrile
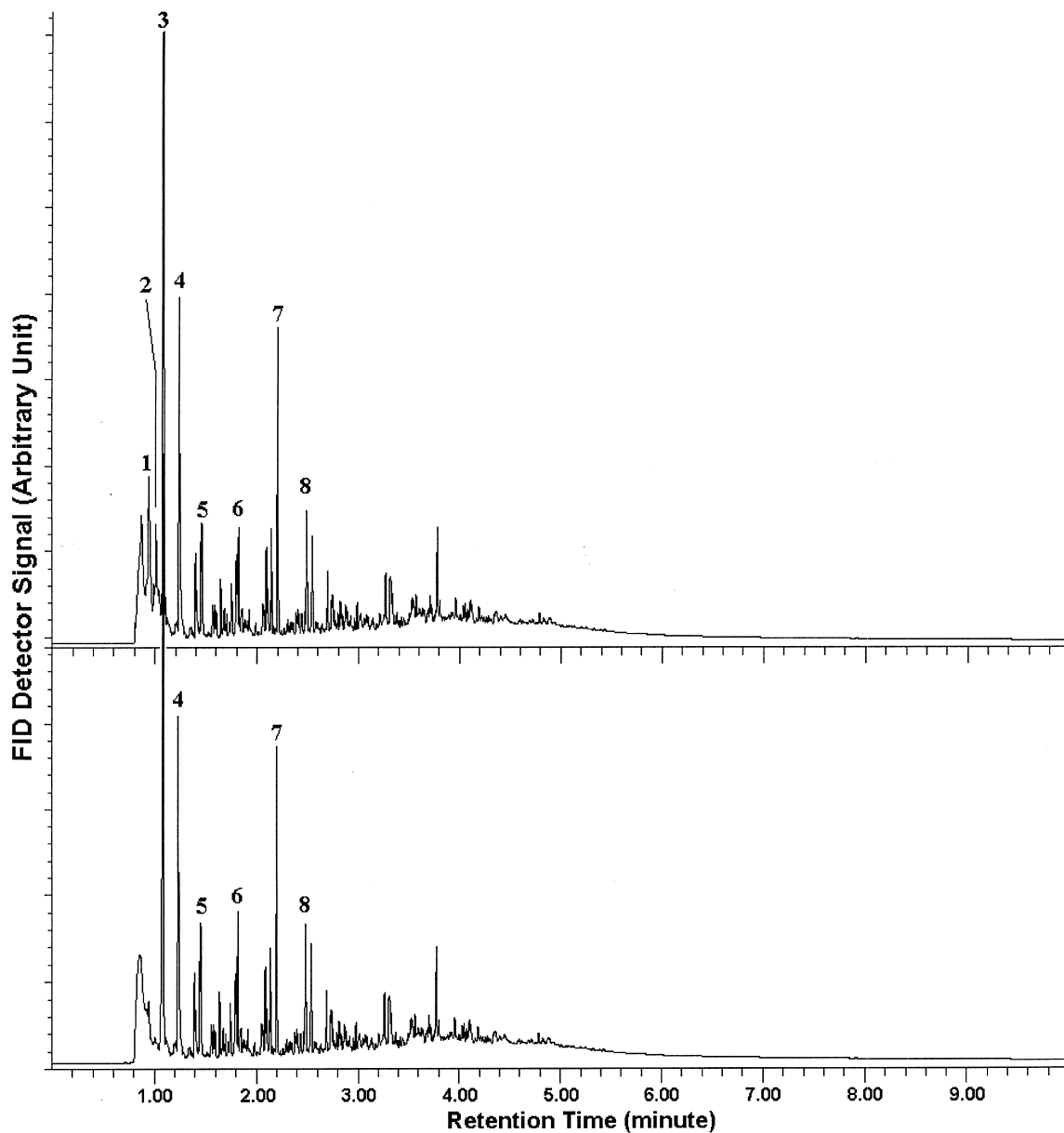


Fig. 9. The pyrogram of nitrile rubber–PVC resin. The nitrile rubber serves as a polymeric plasticizer which polyblend with PVC. The identification of major pyrolysates is (1) butadiene, (2) acrylonitrile, (3) benzene, (4) toluene, (5) xylene, (6) indene, (7) naphthalene, (8) authracene.

rubber–PVC blend compared with pure PVC. The presence of butadiene and acrylonitrile peaks in the blended polymer is an indication of the existence of nitrile rubber.

The other way to lower the volatility of plasticizers is to modify the polymer backbone to become a more flexible plasticizing structure. This can be done by copolymerization with a ''softer'' monomer unit. For example, propylene–ethylene, styrene–butadiene, vinyl chloride–vinyl acetate and styrene–butyl acrylate are all these type of copolymers. Internal plasticization is more permanent but less efficient than conventional ''external'' plasticization by added plasticizer. The analysis of plasticizers in these cases will be just the same as determination of the copolymer composition, where Py–GC has performed effectively on both qualitative and quantitative analysis for years. Fig. 10 shows a pyrogram of a styrene–butyl acrylate copolymer system. The composition as well as microstructure has been determined by Py–GC techniques [10].

## 4. Conclusions

Plasticizers in polymers can be determined by Py–GC simultaneously with polymer composition and microstructure analysis. Most plasticizers can be identified by their mass spectra. The polymeric plasticizers can be resolved by their pyrolysate pattern. The plasticizer that exists as an internally modified polymer backbone can be investigated by analysis of the copolymer composition. Sometimes, the plasticizers can also determined by the thermal desorption method. The key to the successful analysis of plasticizers not only requires a comprehensive understanding of commercial plasticizers but also requires knowledge of the polymer and its applica-
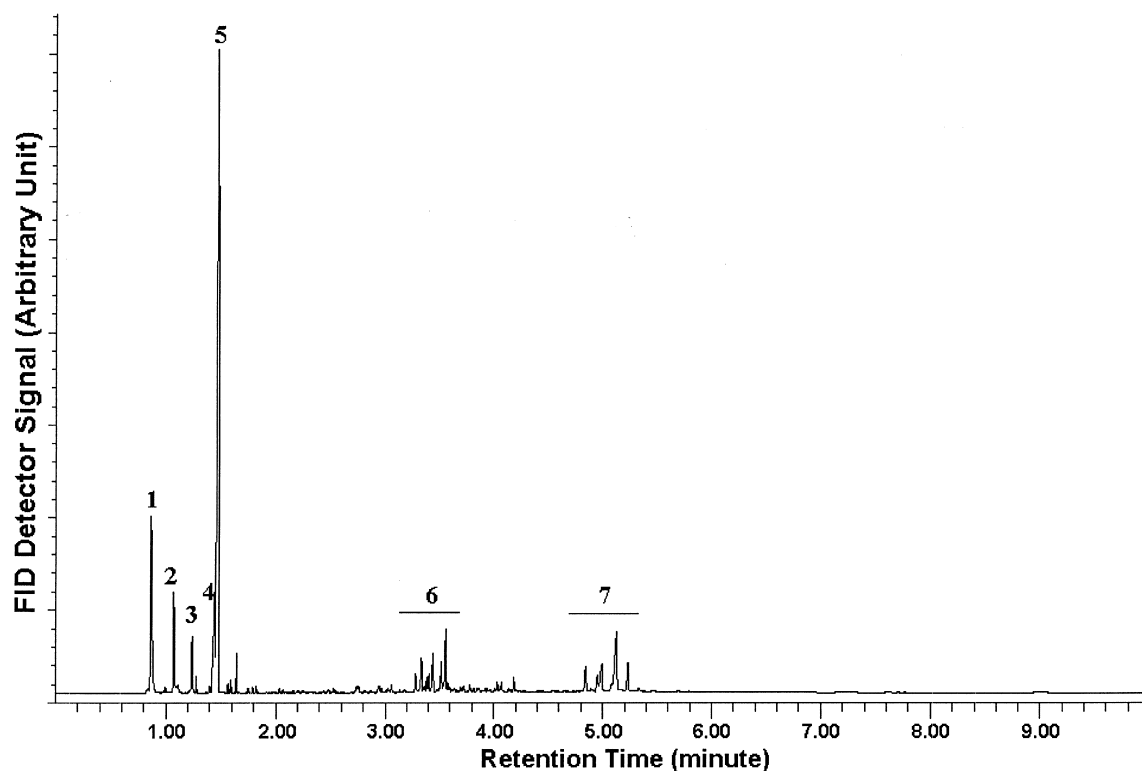


Fig. 10. The pyrogram of styrene–butyl acrylate copolymer. The butyl acrylate serves as internally modifier to modified polystyrene backbone to become a more flexible plasticizing structure. The identification of major pyrolysates is (1) butene, (2) butanol, (3) toluene, (4) butyl acrylate, (5) styrene, (6) styrene–butyl acrylate dimers, (7) styrene–butyl acrylate trimers.

tions. In this study, several examples have been demonstrated to show successful analysis of plasticizers by Py–GC. The most important advantage of Py–GC analysis of plasticizers is that no sample preparation is required and all information can be obtained within one experiment.

# References

[1] R.D. Deanin, in: R.B. Seymour (Ed.), Additives for Plastics, Vol. 1, Academic Press, 1978, pp. 404–408.

[2] J.K. Sears, J.R. Darby, The Technology of Plasticizers, Wiley, New York, 1982.

[3] W.M. Gearhart, F.M. Bell, in: P.F. Bruins (Ed.), Plasticizers Technology, Vol. 1, Reinhold, New York, 1965, Chapter 3.

[4] A.D. Beeler, D.C. Finney, Mod. Plast. Encycl. 56 (No. 10A) (1979–1980) 212.

[5] J. Stepek, H. Daoust, in: Additives for Plastics, Springer-Verlag, New York, 1983, pp. 23–27.

[6] T.R. Crompton, in: Chemical Analysis of Additives in Plastic, Pergamon Press, New York, 1977, pp. 296–341.

[7] C.G. Smith, N.E. Skelly, R.A. Solomon, C.D. Chow, in: G. Zweig, J. Sherma (Eds.), CRC Handbook of Chromatography: Polymers, CRC Series in Chromatography, CRC Press, Boca Raton, FL, 1982, p. 157.

[8] T.P. Wampler, in: T.P. Wampler (Ed.), Analytical Pyrolysis Handbook, Marcel Dekker, New York, 1995, pp. 1–3.

[9] F.C.-Y. Wang, P.B. Smith, Anal. Chem. 68 (1996) 3033–3037.

[10] F.C.-Y. Wang, B.B. Gerhart, P.B. Smith, Anal. Chem. 67 (1995) 3536–3540.

[11] E.A. Collins, J. Bares, F.W. Billmeyer Jr., in: Experiments in Polymer Sciences, Wiley, New York, 1973, pp. 337–345.

[12] M.M. Fares, T. Yalcin, J. Hacaloglu ngor, A. Gungor, S. Suzer, Analyst 119 (1994) 693–696.

[13] J.A. Jansen, J. Philips, Calorim. Therm. Anal. Polym. (1994) 335–352.

[14] J.E. Pittenger, C.F. Cohan, Mod. Plast. 25 (No. 9) (1947) 81.

[15] M.C. Reed, Mod. Plast. 27 (No. 12) (1949) 117.