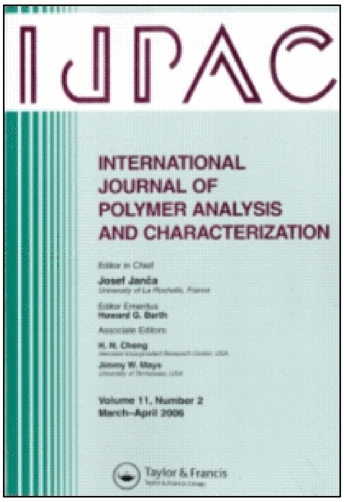

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CHARACTERIZATION OF ACRYLIC RESINS

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Selected samples of commercial acrylic resins used for protection and consolidation of different substrates have been characterized in terms of their chemical structures and compositions. Resin compositions were determined from analysis of the products obtained under controlled thermal decomposition of the samples, whereas the amounts of different components were established by NMR spectroscopy. Several resins were formed by two different structural units, whereas the others contain a third component, although in low quantities. The elution behavior of the samples in adsorption liquid chromatography confirmed that the two-component resins are binary random copolymers. As to the ternary samples, it appears that they are either ternary copolymers or mixtures of two different binary copolymers having one monomeric unit in common. It is also shown that the different protective acrylic resins may be distinguished by their refractive indexes and thermogravimetric behavior.

INTRODUCTION

Polymers based on acrylic and methacrylic esters are largely employed in formulation of varnishes, paints, adhesives, and for protection and consolidation of different substrates, such as wood, bricks, stones, textiles and leather [1,2]. Many types of acrylic resins are available for such purposes, in the form of homopolymers or copolymers and polymer mixtures with two or more components, and the chemical and structural composition of these materials are often not disclosed. To fulfill the needs of end users, these resins must have proper physico-chemical characteristics, such as good film-forming capability, hydrophobicity, permeability to water vapor and environmental stability; all properties strongly dependent on the structural units of the polymer molecules and on their molecular arrangement. The chemical characterization of acrylic resins, particularly in cases when copolymer structures are involved, is therefore an important investigation step necessary to correlate polymer performances with composition.

Copolymers formed by acrylic and/or methacrylic units have similar structural units and normally they cannot be fully characterized by spectroscopic analysis alone. In such cases a good way for structural investigation is to identify the low-molecular-weight products formed in the thermal decomposition of the material, in order to establish the nature

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of the structural units in the polymer, and afterwards determine their amounts with appropriate spectroscopic techniques.

Polymer decompositions may be performed by rapid high temperature pyrolysis of the sample with direct analysis of volatiles in coupled instrumental systems [3,4], or by heating the samples with programmed temperature conditions in systems for thermal volatilization analysis (TVA), in which the evolution of low-molecular-weight products is monitored in the course of the degradation, the volatiles are collected and analyzed. The latter option is generally preferred when mechanisms of degradation are being investigated, because the nature of products can be more easily correlated to the polymer structures than with pyrolysis experiments, in which case the products are formed under drastic conditions that can cause secondary reactions.

In controlled thermal decomposition of polyacrylates, the most abundant products are carbon dioxide and the olefin and alcohol formed from the side-chain ester group. Secondary products are the acrylic monomers, their parent methacrylate units, and the alkane molecules obtained from the ester acrylate groups, in addition to short oligomeric fragments [5–7]. From thermal degradation of lower polyalkylmethacrylates, monomers are obtained in an almost quantitative yield, together with the formation of traces of the olefin corresponding to the ester group, and carbon dioxide [7–9]. With higher methacrylate esters, such as poly(butyl methacrylate), the ester decomposition reaction becomes favored, leading to the formation of higher amounts of olefin molecules, and carbon dioxide, in addition to the monomer [7,9,10]. In acrylic and/or methacrylic block copolymers, thermal decomposition takes place likewise in the homopolymers, with only a change in relative amounts of the different products [9]. From the acrylic units of the copolymers, the production of monomer and of the parent methacrylate ester is higher than that obtained in the decomposition of the corresponding acrylic homopolymers, while the formation of alcohol decreases. The methacrylic units, however, give rise to increased amounts of carbon dioxide and olefins, in comparison with the homopolymer degradations, together with formation of the alcohols from the ester groups.

The decomposition of random acrylate/methacrylate copolymers has been shown to produce mainly the constituent monomers and, as secondary products, both the methacrylic esters parent to the acrylic units and the acrylic esters corresponding to the methacrylic monomers [9]. The ratio between acrylic or methacrylic monomer units and the corresponding parent esters is lower for acrylic component than for the methacrylic one. In addition to the above products, carbon dioxide, alcohol and olefin molecules from the acrylate ester groups, and dimeric structures are also formed in minor amounts.

In general, therefore, the acrylic structural units give always rise, in the degradation process, to the acrylic monomer and the corresponding methacrylic ester, independently of their structural organization; whereas the methacrylic structural units produce the corresponding acrylic esters only when they are part of random copolymers with acrylate units. The different behavior of the methacrylates, in going from homopolymers to block and random copolymers, is also reflected in the decreased amount of monomer formed during thermal degradation [9].

On the basis of the above findings, it is possible to develop a methodology for determining the structure and composition of acrylic resins. In this paper the results of an investigation aimed to the characterization of some commercial acrylic resins, which are employed for protection of different substrates, and have a particular use as consolidants and protectives of works of art [11], are reported. The composition of the different resins has been obtained from analysis of the products obtained under controlled thermal decomposition of the samples, whereas the amount of different components has been determined by NMR spectroscopy. The samples have been preliminarly characterized by SEC (size exclusion chromatography) and FTIR. Refractive index measurements of the polymer samples and thermal characterization by thermogravimetry (TG) also have been performed.

EXPERIMENTAL

Materials

The materials investigated were commercial acrylic resins produced by Rohm and Haas under the trade name of Paraloid, B44, B48N, B66, B72 and B82. All samples, with exception of B66, which is defined a methyl methacrylate-butyl methacrylate copolymer, are generically described as methyl methacrylate or ethyl methacrylate copolymers [12].

As reference samples, the following homopolymer standards (Aldrich, USA) were employed: poly(methyl acrylate) (PMA), (polyethyl acrylate) (PEA), poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), and poly(*n*-butyl methacrylate) (PBMA). Homopolymer mixtures were prepared by dissolution of the proper amounts in acetone and by solvent removal under vacuum.

Thermal Treatment

Polymer thermal decompositions were carried out in a TVA system [13] under vacuum (10^{-4} mbar). Sample size was 100 mg, heating rate 10°C/min from ambient temperature up to 450°C, or to complete sample volatilization. Volatile decomposition products were collected at liquid nitrogen temperature in glass cells from which samples could be extracted with a gas-tight syringe, and injected into a Hewlett-Packard HP5890A gas chromatograph interfaced with a Hewlett-Packard 5970 quadrupole mass spectrometer. Separations were obtained on a HP1 semicapillary column, 12 m × 0.2 mm × 0.33 μm (stationary phase: cross-linked methyl silicone resin), with the following temperature program: 2 min at 30°C, ramp to 200°C at 20°C/min.

Thermogravimetric measurements were run on a DuPont 951 thermobalance, under nitrogen flow of 60 cm^3/min and a heating rate 10°C/min.

NMR Spectroscopy

Spectra were measured on a Jeol EX400 instrument, operated at 400MHz for the proton spectra and at 100 MHz for the ^{13}C spectra (flip angle: 45°, 11000 pulse and repetition time: 0.6 s). Polymer samples were dissolved in deuterated chloroform, using tetramethylsilane as an internal reference.

Characterization Techniques

Molecular weight distributions were determined with a modular SEC systems, made of a Waters M45 pump, a Rheodyne 7161 injection valve with 150 μL sample loop, and an Erma ERC 7510 differential refractometer. Elution was in distilled tetrahydrofuran, at 1

cm^3/min flowrate. Four separation columns (PL-Gel, Polymer Labs, UK), 5-μm particle diameter and 500, 10^3, 10^4, 10^5° nominal porosity were employed.

HPLC separations were obtained on a Bruker LC21 liquid chromatograph, with a 50 × 4.6 mm column packed with Develosil Si30 silica gel (5-μm particle size and 30 Å pore diameter) and a DDL21 evaporative light scattering detector (Eurosep Instruments France). The detector setting was 45 °C for the nebulization chamber, and 500 for the photomultiplier sensitivity. HPLC was performed at 0.5 cm^3/min flowrate, with a solvent gradient from toluene/methyl ethyl ketone (98/2) to pure methyl ethyl ketone in 27 min. With the above combination of experimental conditions, the separation mode was adsorption according solute polarity. SEC and HPLC data were acquired and processed on an Olivetti M300 PC with a Bruker Chromstar software.

FTIR spectra were measured on a Perkin Elmer 1710 instrument, at 4 cm^{-1} resolution, with a DTGS detector. The samples were polymer films cast onto KBr pellets.

Refractive indexes were determined with an Abbe refractometer on 50-μm polymer films prepared by pressure molding at 150°C.

RESULTS AND DISCUSSION

Molecular Characterization

Molecular weights of reference homopolymers and of Paraloid resins were determined by SEC as apparent values, calculated with a PMMA calibration. Weight- and number-average molecular weights, M_w and M_n, respectively, are reported in Table I, together with dispersity indexes M_w/M_n.

FTIR Characterization

Infrared spectra of the homopolymers and of the Paraloid resins show characteristics absorptions in the C-H stretching region (2900–3000 cm^{-1}), the carbonyl stretching at ~ 1730 cm^{-1}, peaks due to C-H bending at ~ 1450 and 1385 cm^{-1}, and the multiple absorp-

TABLE I

Molecular weights of reference homopolymers and of Paraloid resins

Sample	M_w (10^{-3})	M_n(10^{-3})	M_w/M_n
PMA	37	12	3.08
PEA	106	35	2.60
PMMA	85	48	1.77
PEMA	328	146	2.28
PBMA	257	92	2.79
B44	105	23	4.56
B48N	184	48	3.83
B66	55	27	2.04
B72	88	41	2.15
B82	96	38	2.53

tions due to the C-O stretching between 1300 and 1150 cm^{-1}. The latter region allows the discrimination between acrylates and methacrylates [14], as methacrylic units show a doublet at 1250 cm^{-1}, whereas the acrylic ones present in the same region a single broad peak. Spectra of Paraloids reveal in some cases a more complex pattern, apparently due to the simultaneous contributions from both types of structures. In any case infrared characterization does not allow the exact identification of structural units, but only indications about the type of components.

Qualitative Analysis

The volatile products obtained in the thermal degradation under vacuum of the Paraloid resins and of the reference homopolymers were separated and analized by GC-MS. The results relative to the reference homopolymers are reported in Table II.

As expected, from methacrylic homopolymers only the corresponding monomers were obtained, with the exception of PBMA, which showed the presence of butanol and 1-butene also, as a result of the ester group decomposition. The acrylic homopolymers, in addition to the corresponding monomers, always gave the parent methacrylic esters and the alcohol molecules deriving from the ester group. In the case of PMA, the methyl ester of oxiranic acid was found also.

To investigate the effects of the simultaneous decomposition of methacrylic and acrylic ester units belonging to different polymer chains, a series of mixtures was heated to complete volatilization. As an example, from a 50/50 mixture of PBMA and PMA, 1-butene, butanol, BMA, MA, MMA and carbon dioxide were obtained. In all the cases the results showed that the mixture behavior basically reflects that of the single components, yielding carbon dioxide, acrylic monomer, parent methacrylic ester, olefin and alcohol from the polyacrylate decomposition, and mainly methacrylic monomer from the polymethacrylate part.

In Figure 1 the gas chromatogram of the degradation products obtained from sample B72 is shown. The most abundant peaks are those of ethyl methacrylate (EMA), at 2.3 min and of methyl acrylate (MA), at 0.53 min. Methyl methacrylate (MMA), at 1.1 min, can be considered to be a secondary product originated from the MA units, and the same applies to ethyl acrylate (EA) eluting at 0.98 min, in connection with the EMA units. Butyl methacrylate (BMA) at 7.2 min, and the very low amount of butyl acrylate (BA) at 5.6 min, appear to be related in the same way. This pattern is fully compatible with a copolymer system where EMA, MA and BMA are the structural units in the macromole-

TABLE II

Volatile decomposition products of the reference homopolymers

Sample	Main products	Secondary products
PMA	methyl acrylate, methanol, carbon dioxide, oxirane acid methyl ester	methyl methacrylate
PEA	ethyl acrylate, ethanol, carbon dioxide	ethyl methacrylate
PBA	butyl acrylate, butanol, carbon dioxide	butyl methacrylate
PMMA	methyl methacrylate, carbon dioxide	
PEMA	ethyl methacrylate, carbon dioxide	
PBMA	butyl methacrylate, butanol, carbon dioxide	1-butene

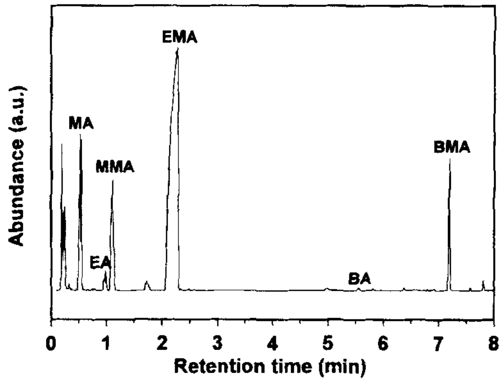


FIGURE 1 GC of degradation products from B72 resin.

cules. The presence of ethanol at 0.34 min is also in agreement with such conclusions. The peak eluting at 1.74 min is due to toluene which is present in the sample, probably as solvent residue from the polymerization [15]. However, very low amounts of toluene were also found in the degradation of B72 samples previously heated at 100°C under vacuum, until all volatile compounds present in the resin would be eliminated. Some toluene, therefore, is likely to come from initiator residues at the chain ends.

In Figure 2 the chromatographic separation of products formed in the degradation of B44 resin is reported. The same compounds which were found in the previous case are present, but relative abundances are different. MMA is the most abundant product and can be taken as one of the resin components; EA and BMA appear to be the others. The same constituents were found also in the B82 sample.

B66 and B48N samples showed the same degradation products, 1-butene (0.26 min), butanol (0.8 min), MMA (1.1 min) and BMA (7.2 min), as seen from Figure 3 where the chromatogram of the products obtained from B66 is reported. It is straightforward to conclude that both MMA and BMA units are present in the two resins. The same products, however, would be formed in the decomposition of either a mixture of the two methacrylic homopolymers or in that of a binary MMA-BMA copolymer. To answer this question HPLC analysis was applied. In Figure 4 the chromatogram of a mixture of PMMA and PBMA is reported, where the peaks of the two polymers are completely separated. In the same figure, the chromatograms of the two Paraloid samples show, in each case, only one peak eluting with intermediate retention times, as compared with the homopolymers, thus confirming the copolymeric nature of the resins. The elution pattern of the two copolymers reflects their different compositions and possibly different copolymer heterogeneities: in particular, the broad peak of B48N, which has a high MMA content, could be due to a wide chemical composition distribution across the polymer.

In the case of the three component resins, B72, B44 and B82, the same decomposition products would come from random terpolymer structures or from mixtures of particular binary copolymers. For example, a mixture of EMA-MA and MA-BMA random copolymers for sample B72, or mixtures of MMA-EA and EA-BMA for B44 and B82. Due to the low amount of BMA units in the resins, and to the multiple composition combinations which are possible, it is difficult to determine which is the molecular organization of the different structural units in these resins. The HPLC analysis of the samples, in conditions

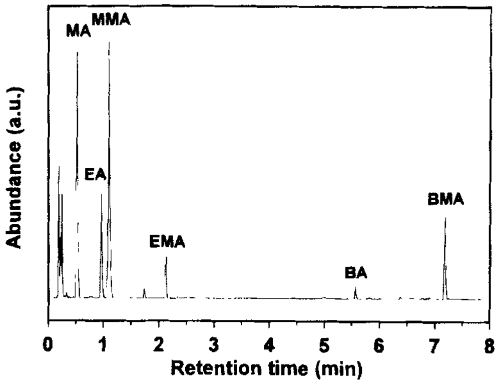


FIGURE 2 GC of degradation products from B44 resin.

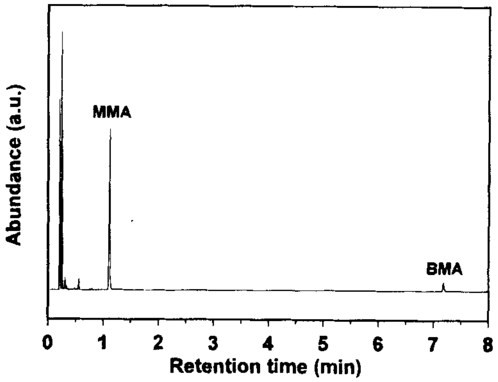


FIGURE 3 GC of degradation products from B66 resin.

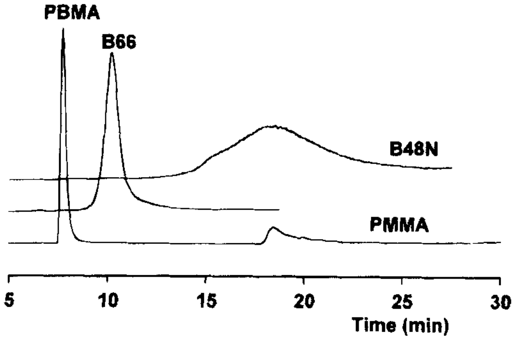


FIGURE 4 HPLC chromatograms of B48N, B66 and mixture containing PBMA and PMMA. For elution conditions see text.

where the homopolymers in equivalent mixtures were well separated, showed in B72 a small peak eluting earlier than the principal one (Figure 5). The retention time of the latter, eluted in the range of peaks of PEMA and PMA, and is compatible with that of a EMA-MA copolymer, whereas the former peak at ca. 10 min could well be due to a BMA-MA copolymer. It cannot be excluded, therefore, that the sample B72 be formed by a binary copolymer as a main component, and a small amount of a second copolymer, with one common structural unit.

Similar considerations apply to B44 and B82 samples. The HPLC separation results of Figure 6, in fact, show for B82 a principal peak, which could be due to an EA-MMA copolymer, and a very small peak at retention times between those of PBMA and PEA, compatible with a BMA-EA copolymer elution.

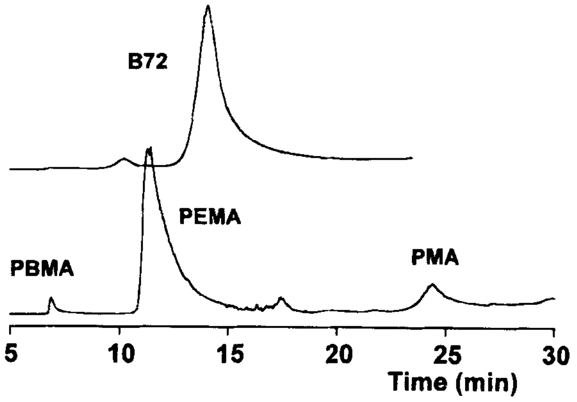


FIGURE 5 HPLC chromatograms of B72 and mixture containing PBMA, PEMA and PMA. For elution conditions see text.

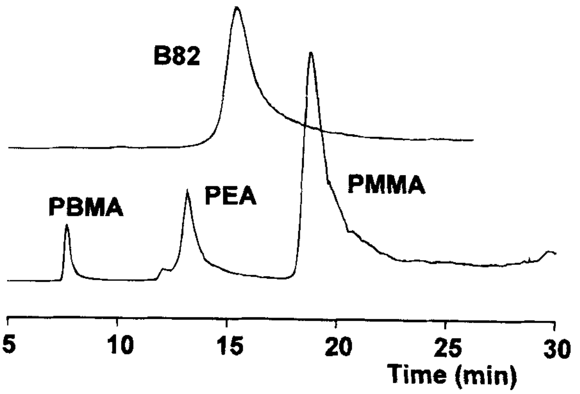


FIGURE 6 HPLC chromatograms of B82 and mixture containing PBMA, PEA and PMMA. For elution conditions see text.

Quantitative Analysis

Quantitative composition of samples B48N and B66 could be directly determined with ^{1}H-NMR, by integration of proton signals from -O-CH_3 groups, at 3.6 ppm, and from -O-CH_2-, at 3.97 ppm. In the case of samples with three different structural units combination of ^{1}H-NMR and ^{13}C-NMR measurements was applied. As an example, from the ^{1}H-NMR spectrum of B72, shown in Figure 7, the content of MA units (32%) and of combined EMA+BMA (68%) was measured. The separation of contributions from the two methacrylate components was accomplished by analysis of the ^{13}C spectra.

The ^{13}C spectrum of B72 resin is reported in Figure 8. All the peaks could be assigned on the basis of the spectra measured on the reference homopolymers, and of data from ref. [16]. The results, relative to the different acrylate and methacrylate units, are given in Table III.

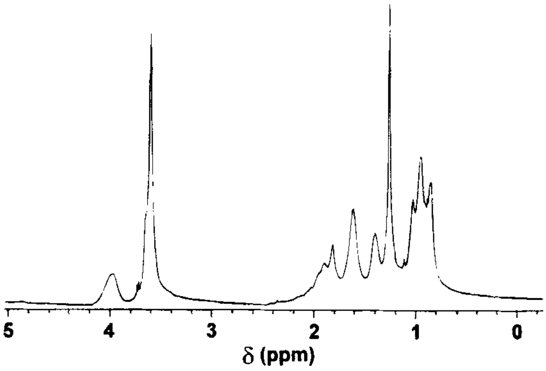


FIGURE 7 ^{1}H-NMR spectrum of B72.

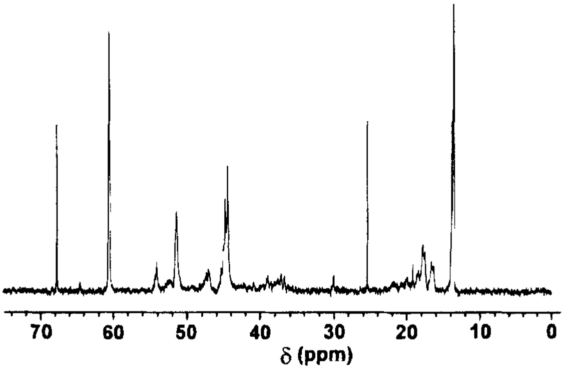
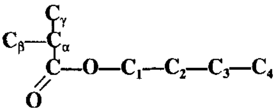


FIGURE 8 ^{13}C-NMR spectrum of B72.

TABLE III

^{13}C-NMR chemical shifts of acrylic polymers



			δ(ppm)		
	MA	EA	MMA	EMA	BMA
C_1	51.6	60.4	51.2	60.8	64.6
C_2	–	13.9	–	13.6	30.1
C_3	–	–	–	–	16.3
C_4	–	–	–	–	13.6
C_α	40.9–41.1	40.8–41.1	44.5–45.2	44.6–45	44.6–44.9
C_β	35	35	50–53.9	54.5	54
C_γ	–	–	17.2–21.8	18.1	19.1
CO	174–175	174–175	175–177	176–178	175–178

The amount of BMA, compared to the EA units in samples B44 and B82, and to the EMA units in sample B72, has been evaluated from the ratios of the integrated signals relative to the C1 carbons in the different samples. In the experimental conditions employed for spectra acquisition, the nuclear Overhauser effect was not completely eliminated and therefore the results obtained have some inaccuracy. However, due to the low amounts of BMA units to be measured and to the inherent errors in the measurement of small peaks, it was preferred to run spectra acquisitions in conditions of higher sensitivity. As a result, the overall amount of BMA in sample B72 was determined to be 2.2 mol %, whereas those of samples B44 and B82 were estimated to be of the order of 1 mol % each. These low quantities are in agreement with the qualitative indications previously obtained from the GC-MS spectra.

The complete composition results obtained for the Paraloid samples are reported in Table IV.

Refractometric Measurements

Measurements of refractive index have been reported in the past for characterization of Paraloid B72 resin [17], showing that the value of the copolymer is intermediate between those of the two homopolymers PEMA and PMA. In the case of copolymers and of polymers mixtures, it is known that refractive indexes are linearly related to their compositions according to the relationship: $n = \Sigma\, w_i\, n_i$, where w_i and n_i are weight fraction of component i and refractive index of homopolymer i, respectively [18].

Refractive indexes of the Paraloid resins and of the acrylate and methacrylate homopolymers have been measured and compared with those calculated on the basis of their weight compositions, as obtained from data of Table IV. The results are reported in Table V, where it may be seen that there is a good agreement between calculated and experimental values. However, the small differences between refractive indexes of the different polymers makes it difficult to use these type of measurement for characterization purposes.

TABLE IV

Composition of the Paraloid resins, mol %.

Sample	MA	EA	MMA	EMA	BMA
B44	–	~28	70.3	–	~1
B48N	–	–	74.5	–	25.5
B66	–	–	47.6	–	52.4
B72	32.0	–	–	65.8	2.2
B82	–	~43	56.1	–	~1

TABLE V

Refractive indexes and maximum volatilization rates of the Paraloid resins

Sample	*n* measured	*n* calculateded	T_{max}(°C)	
B44	1.4790	1.4743	305	405
B48N	1.4807	1.4824	305	400
B66	1.4785	1.4792	290	380
B72	1.4756	1.4743	340	370
B82	1.4766	1.4766	325	400

Thermal Characterization

The thermal behavior of the Paraloid resins shows distinct differences among the samples, which reflect both polymer compositions and the molecular arrangements of the structural units on the degradation reactions. The derivative weight loss curves (DTG) relative to treatment under nitrogen up to 600°C, are plotted in Figure 9. The temperatures of maximum volatilization rate, T_{max}, for the different degradation steps, are reported in Table V.

The decomposition process is influenced by the copolymer structures and by their compositions, as it can be revealed by comparison of the experimental TG curves with the weight loss curves obtained from homopolymer mixtures having the same composition as the Paraloid resins. In Figure 10 these curves are reported for B48N and B66. The samples are formed by the same structural units, MMA and BMA, and the former is reacher in MMA than the latter. B48N weight loss appears very much similar to that of the mixture, whereas the decomposition of B66 takes place earlier than that of the corresponding mixture. The reason may be that with the higher amount of BMA units in B66 sample, the chain scissions mostly take place at BMA sequences, from which depolymerizations may start and proceed even through the MMA units, at temperatures lower than those producing the scission of MMA-MMA bonds.

The TG curves of samples B44 and B82, formed by the same structural units, are reported in Figure 11, and compared with those of the corresponding homopolymer mixtures. The experimental weight losses are very similar for the two resins, in spite of their composition difference and copolymer decompositions take place earlier than those of the mixtures.

In the case of B72, Figure 12, a large stabilization effect is seen, in comparison with the mixture. To explain this behavior it may be tentatively suggested that the depolymerization of EMA sequences is drastically reduced by the presence of the MA units in the polymer chains.

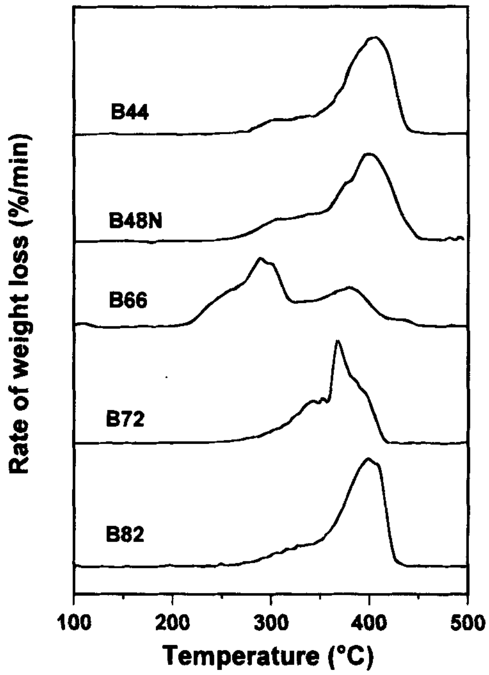


FIGURE 9 Derivative weight loss curves of the acrylic resins heated under nitrogen flow at 10°C/min.

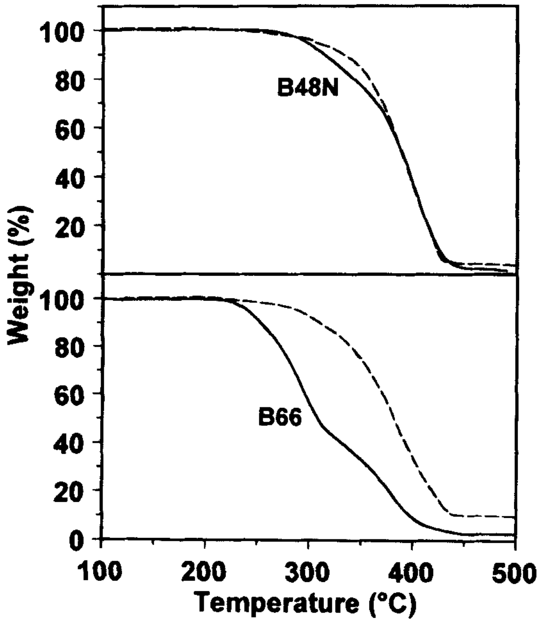


FIGURE 10 Comparison between thermogravimetric curves of B48N and B66 resins (solid lines), with weight loss curves obtained from the equivalent homopolymer mixtures (dashed lines).

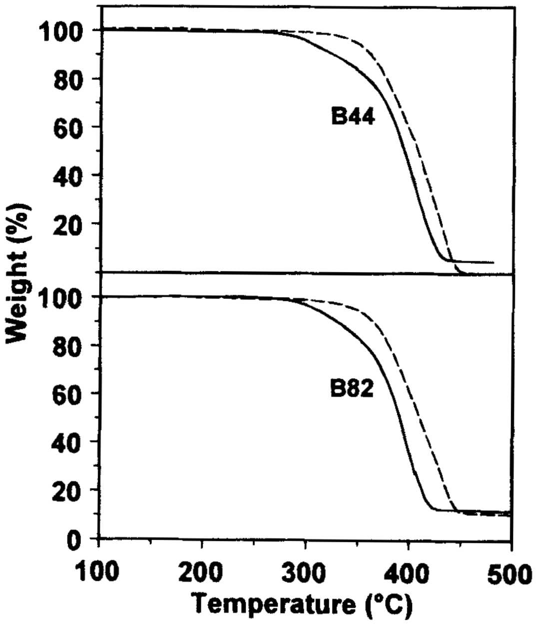


FIGURE 11 Comparison between thermogravimetric curves of B44 and B82 resins (solid lines), with weight loss curves obtained from the equivalent homopolymer mixtures (dashed lines).

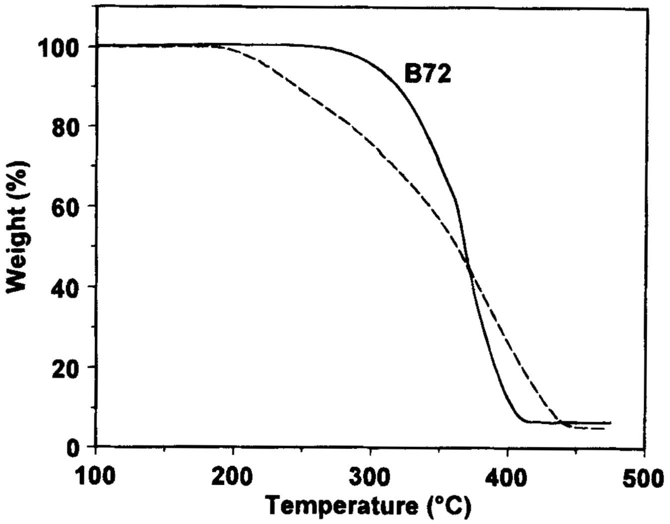


FIGURE 12 Comparison between thermogravimetric curve of B72 resin (solid line), with weight loss curve obtained from the equivalent homopolymer mixture (dashed line).

CONCLUSIONS

The chemical constituents of protective resins containing acrylic and/or methacrylic units could be identified through analysis of the products formed by thermal degradation of the resins. In order to distinguish between primary and secondary degradation products, and therefore correctly interpret the results, the knowledge of the degradation mechanisms of acrylic polymers, and of their mixtures and copolymers, is necessary. It is also possible, in most cases, to distinguish between a copolymer and a polymer blend, on the basis of different degradation patterns. However, when no clear discrimination between these two situations arises from the nature of decomposition products, adsorption liquid chromatography of the samples may give the proper indications by comparing the elution characteristics of the material with those of homopolymer mixtures having equivalent chemical compositions.

The investigated resins have been found to be binary copolymers and ternary systems, where the third structural unit is present in fairly low amounts. Although the results are not unequivocal, it seems that the ternary resins were formed by blending two binary copolymers which have one common monomeric unit.

Refractometric and thermal characterization of the resins showed patterns in agreement with their chemical compositions, demonstrating the possibility of using such measurements for differentiating among different products.

Acknowledgments

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