

Investigation of Polyesters by Time-of-Flight Secondary Ion Mass Spectrometry

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Abstract: The structural characterization for series of polyesters has been done by time-of-flight secondary ion mass spectrometry (TOF-SIMS). Polymer fragments and intact oligomers composed of large numbers of repeat units have been investigated. Transesterification of polyesters in trifluoroacetic acid (TFA) and chlorodifluoroacetic acid (CFA) was monitored and reaction products were identified using TOF-SIMS. The shapes and intensities of clusters in transesterification spectra show good agreement with the theoretical isotope pattern. TOF-SIMS spectra were used to obtain information about the progress of the transesterification reaction.

Keywords: time-of-flight, secondary ion mass spectrometry, polyester, transesterification

1. Introduction

The thermal decomposition mechanisms of several polyesters were studied by direct pyrolysis mass spectrometry, using low-energy electron ionization and chemical ionization.^{1,2} These studies reported the predominant thermal fragmentation mechanisms of polyesters. Since its introduction in 1981, fast atom bombardment mass spectrometry (FAB-MS) has become widely used for the analysis of high molecular weight and

thermally labile compounds. A limited investigation of polyesters and polyamides was done in the low mass range using FAB-MS.³

Mass spectrometry has become a valuable technique for characterization of synthetic polymers in the high mass range. This technique provides the molecular weight distribution, data on the sequence of repeat units, polymer additives and impurities, and structural information. Many ionization methods have been applied in the structural characterization of high molecular weight

polymers. They include field desorption,^{4,5} fast atom bombardment,⁶ electrohydrodynamic ionization,^{7,8} plasma desorption,⁹ electrospray ionization,¹⁰ and matrix-assisted laser desorption/ionization (MALDI)^{11,12} mass spectrometry. Of these methods, secondary ion mass spectrometry (SIMS) in combination with time-of-flight (TOF) mass analyzers has been used for structural characterization of various polymers.¹³⁻¹⁵ The masses of the repeat unit and terminal groups and molecular weight distributions of polymers have been determined from their TOF-SIMS spectra. TOF-SIMS provides good sensitivity and structural specificity for high mass ions so that intact oligomers and large polymer fragments are observed.

The purpose of the present investigation was detailed analysis of the oligomers and fragment ions of polyesters and the transesterification products of polyesters with trifluoroacetic acid or chlorodifluoroacetic acid. The progress of such reactions was monitored, and reaction products were identified using TOF-SIMS.

2. Experimental

2.1 Instrument

A time-of-flight secondary ion mass spectrometer (TOF-SIMS) was used to obtain mass spectra of the polyesters.^{16,17} It has high transmission and detects ions in the mass range m/z 1-10,000 simultaneously. A continuous beam of primary argon ions is produced in a conventional electron impact source. The ions are accelerated to 10 KeV and are focused by slit electrodes.

Secondary ions are extracted from the sample and accelerated by an ion lens operating at 3 kV into a time-of-flight (TOF) mass analyzer. The TOF uses a reflectron to reduce line widths and has a total flight path of 2 m.

The detector is combined with a channel plate which converts an ion into many electrons, a scintillator which functions by

converting the electrons into photons, and a photomultiplier.

The recording system consists of a multistop time-to-digital converter (TDC), a fast buffer memory, and an accumulating memory board.

2.2 Sample Preparation

The following polymer samples were obtained from Aldrich Chemical Co. (Milwaukee, WI): poly(ethylene succinate), poly(ethylene adipate), poly(neopentyl glycol sebacate). The source of poly(trimethylene adipate) and poly(butylene adipate) was Polysciences, Inc. (Warrington, PA). Poly(trimethylene succinate) and poly(trimethylene glutarate) were obtained from Scientific Polymer Products, Inc. (Ontario, NY). TOF-SIMS spectra of polyesters were obtained from thin polymer films cast from solutions of polyesters in *N,N*-dimethylformamide (DMF) on a silver substrate. Transesterification of polyesters was carried out by dissolution in trifluoroacetic acid (TFA) or chlorodifluoroacetic acid (CFA) and allowing the reaction to occur for a specific time. The concentrations of polymers in DMF, TFA and CFA solutions were in the range of 1-2 mg/ml. After transesterification 1-5 μ L of solution were deposited onto ca. 20 or 80 mm² of silver target. Approximately 1-2 μ g of each polyester was deposited on the silver substrate for analysis.

3. Results and Discussion

3.1 Polyester TOF-SIMS Spectra

TOF-SIMS spectra of the polyesters studied were obtained in the mass range m/z = 1-3500. The peaks in the spectra can be resolved into three well-defined series: oligomer; repeat unit; and fragmentation series. Desorption of intact polyesters generate the oligomer series. The repeat unit series consists of an integral number of ester repeat units. Formation of large fragment ions from

polyesters involves chain-breaking events to produce fragment molecules.

TOF-SIMS positive ion spectra of poly(ethylene succinate), poly(trimethylene succinate), poly(trimethylene glutarate), poly(ethylene adipate), poly(trimethylene adipate), poly(butylene adipate), and poly(neopentyl glycol sebacate) were studied. Interpretation of the spectra will focus on the information they provide for structural characterization. A segment from a typical spectrum of poly(ethylene adipate) in the mass range $m/z = 0-600$ shows the dominant peaks which are $C_2H_3^+$ (m/z 27), $C_2H_5^+$ (m/z 29), $C_3H_5^+$ (m/z 41), $C_3H_7^+$ (exact mass m/z 43.0548), $C_2H_3O^+$ (exact mass m/z 43.0184), $C_4H_7^+$ (exact mass m/z 55.0548), $C_3H_3O^+$ (exact mass m/z 55.0184), $C_4H_9^+$ (exact mass m/z 57.0704) and $C_3H_5O^+$ (exact mass m/z 57.0340). Na^+ (m/z 23) and K^+ (m/z 39) ions are also found in the spectra as well as Ag^+ (m/z 107 and 109) from the substrate. The other peaks in the lower mass range are due to carbon-, oxygen-, and hydrogen-containing ions which are found in the positive spectra of nearly all polymers. Silver clusters (Ag_2^+ , Ag_3^+ , etc.) and uncationized repeat unit ions are also found in this low region. For example, the spectrum of poly(ethylene adipate) shows Ag_2^+ (m/z 214), Ag_3^+ (m/z 321) and a peak of moderate intensity at m/z 173 which can be attributed to monomer, $R+H$ (R = repeat unit). There are also peaks corresponding to dimer $2R+H$, trimer $3R+H$, tetramer $4R+H$, etc at m/z 345, 517, and 689, respectively with decreasing intensities. Fragment ions from the repeat units are found at m/z 99, 155, 271, and 389. These ions are characteristic for the structure of the repeating units of poly(ethylene adipate). The same similarity is found in the low mass range of the other polyester spectra.

Fig. 1(A) shows the TOF-SIMS spectrum of poly(ethylene adipate) in the mass range $m/z = 600-2000$. One example of cluster structures is also shown in Fig. 1(B). Peaks of the oligomer and repeat unit series of poly(ethylene adipate) are labeled O_{EA} and R_{EA} ,

respectively. The peaks observed in the spectra are due to oligomers and repeat units cationized with both Ag^+ and Na^+ . The oligomer series consists of an integral number of repeat units, two terminal groups and the metal cation. The repeat unit series comes from the integral number of the repeat unit plus the mass of the metal cation.

The repeat unit series, corresponding to $[nR + M]^+$ where R = repeat unit and $M = Ag$ and Na , results from fragments produced by cleavage of the COO bond along the polymer backbone. There are pairs of peaks having a mass difference of $\Delta m/z = 84$, the mass difference between Na and Ag . The spacing between consecutive peaks involving the same cation in the oligomer or repeat unit series is the same mass as the repeat unit of polyesters. For example, in the oligomer series of poly(ethylene adipate) for $M=Ag$, the mass difference between peaks for $n=4$ at $m/z = 857$ and $n=5$ at $m/z = 1029$ is equal to $\Delta m/z = 172$, the mass of the repeat unit of poly(ethylene adipate). The mass difference between oligomer series peaks and repeat unit series peaks, which have the same metal cation, are the combined masses of the terminal groups of polyesters. For example, the mass difference between the O_{EA} peak at $m/z = 1029$ and 1031 ($n=5$, $M=Ag$) and the R_{EA} peak at $m/z = 967$ and 969 ($n=5$, $M=Ag$) is equal to $\Delta m/z = 62$, the combined masses of H and $O(CH_2)_2OH$.

3.2 Transesterification of Polyesters in Trifluoroacetic Acid

TOF-SIMS spectra of polymers are obtained from polymer solutions deposited on a silver substrate. If polymers are insoluble or of high molecular weight it is difficult to characterize them using the TOF-SIMS techniques. For intractable or high molecular weight polymers, selective cleavage reactions or chemical derivatization could be used if they occur at specific bonds, do not change the structure of the polymer, and produce chain segments that are large enough to contain information about more than one

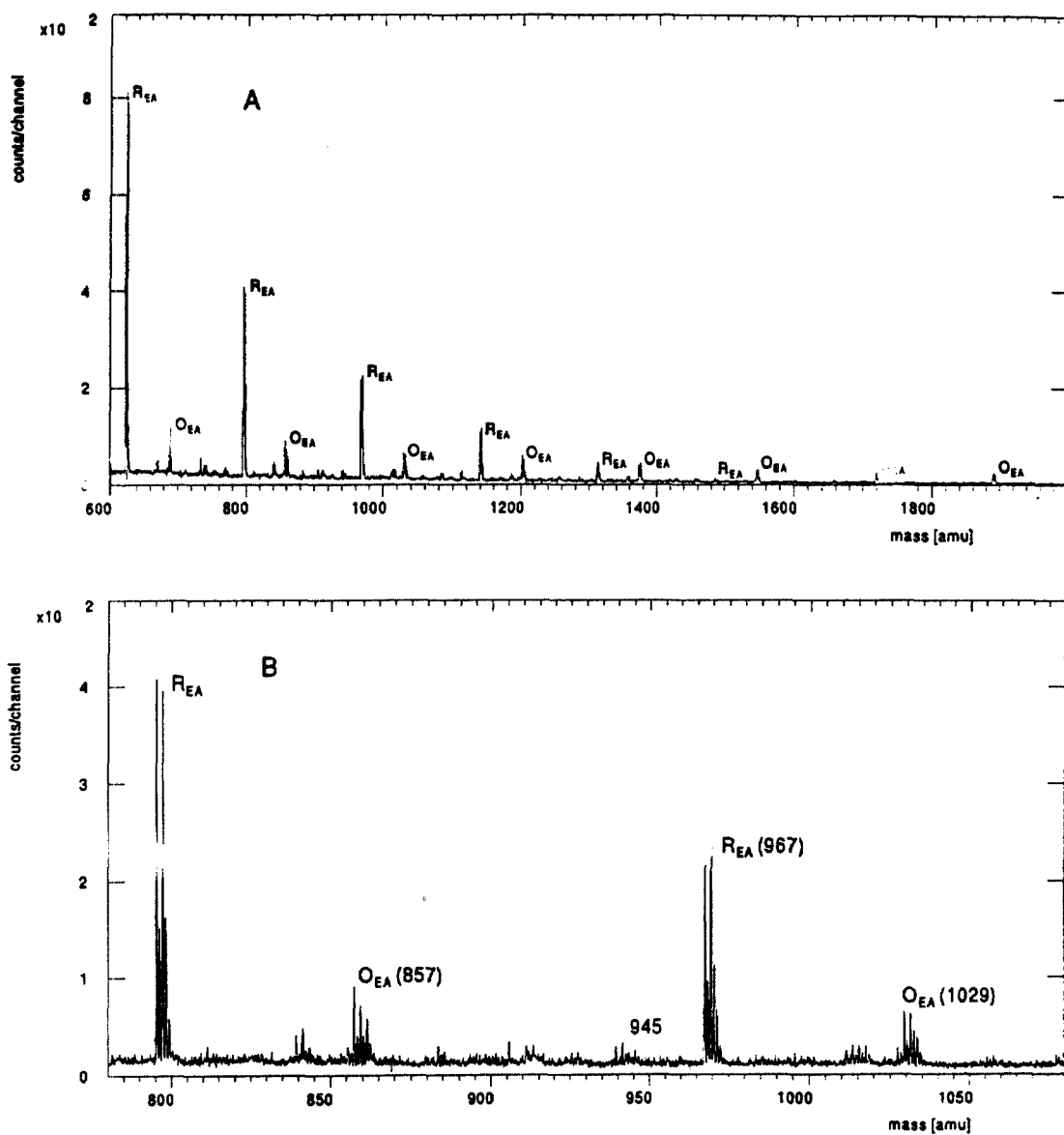


Fig. 1 Positive-ion TOF-SIMS spectrum of poly(ethylene adipate) in the mass range (A) $m/z = 600-2000$ (B) $m/z = 780-1080$.

repeat unit. These reactions can be used to cleave specific bonds of intractable polymers or modify polymers by incorporating desirable chemical functions in the backbone. Studies on polyurethanes have demonstrated that transesterification can be used to selectively break bonds in copolymers.¹⁸ The feasibility and progress of such reactions can be monitored by using TOF-SIMS.

Transesterification of polyesters in trifluoroacetic acid (TFA) occurs at ester bonds and produces diesters of TFA and diols in polyesters. Products were identified from TOF-SIMS spectra of polyester thin films cast from TFA solutions. Fig. 2 shows a spectrum of the transesterification products of poly(ethylene adipate) and TFA in the mass range m/z 500-2100 after 8 hours of reaction. Diester ions of poly(ethylene adipate) labeled T_{EA} , while repeat unit peaks of poly(ethylene adipate) are labeled R_{EA} . Peaks of the oligomer for poly(ethylene adipate) are not observed in the spectrum after the reaction.

The T_{EA} ions arise from diesters of the diol and TFA. They consist of an integral number of polyester repeat units plus an additional ethanediol and two trifluoroacetates at the diol ends. The spacing between consecutive T_{EA} peaks involving the same cation corresponds to the mass of the repeat unit of poly(ethylene adipate). For example, in the T_{EA} series of poly(ethylene adipate) for $M=Ag$, the mass difference between peaks for $n=4$ at $m/z = 1049$ and $n=5$ at $m/z = 1221$ is equal to $\Delta m/z = 172$, the mass of the repeat unit of poly(ethylene adipate).

Transesterification of polyesters was carried out in TFA for different reaction times. In order to get information about the progress of the transesterification reaction, TOF-SIMS spectra of poly(butylene adipate) were taken after 15 minutes, 1, 3, and 8 hours, respectively. The main peaks and relative intensities in the mass range m/z 700-1000 for different reaction times are tabulated in Table I. The oligomer series

peaks ($n=3$ and $n=4$) still exist in the spectrum taken immediately after poly(butylene adipate) was dissolved in TFA. However, they have disappeared in the spectrum for 3 hours of reaction: the relative intensities of diester ions have increased after 3 hours of reaction. The increasing abundance of two tagged ions indicates that the reaction has progressed with the time.

3.3 Transesterification of Polyesters in Chlorodifluoroacetic Acid

Transesterification with trifluoroacetic acid labels the alcohol part of the ester linkage and the mass of the CF_3CO group ($m/z = 97$) was used as a mass marker. Chlorodifluoroacetic acid was also investigated as a transesterification reagent for polyesters to take advantage of its unique isotope clusters. The $CClF_2CO$ ($m/z = 113$) group in chlorodifluoroacetic acid provides a good mass marker and cleaved fragments can readily be identified because of the chlorine isotope patterns.

When the peaks are weak, or the high mass fragments are not well-resolved, it is helpful to compare the spectrum of TFA transesterification and that of CFA transesterification for the same polyester. The mass difference between peaks including one CF_3CO group ($m/z = 97$) and peaks including one $CClF_2CO$ group ($m/z = 113$) is 16, and the mass difference of two labeled fragments is 32. Therefore, the peaks can be easily identified as the mass difference between them is 0 for not tagged, 16 for one-tagged and 32 for two-tagged fragments.

Transesterification of polyesters in chlorodifluoroacetic acid cleaves selectively the ester bond and produces diesters of chlorodifluoroacetic acid and diols in polyesters. Fig. 3 shows spectra of poly(ethylene adipate) after transesterification with chlorodifluoroacetic acid for 11 hours in the mass range m/z 600-2000. Chlorodifluoroacetates of poly(ethylene adipate) are labeled C_{EA} and

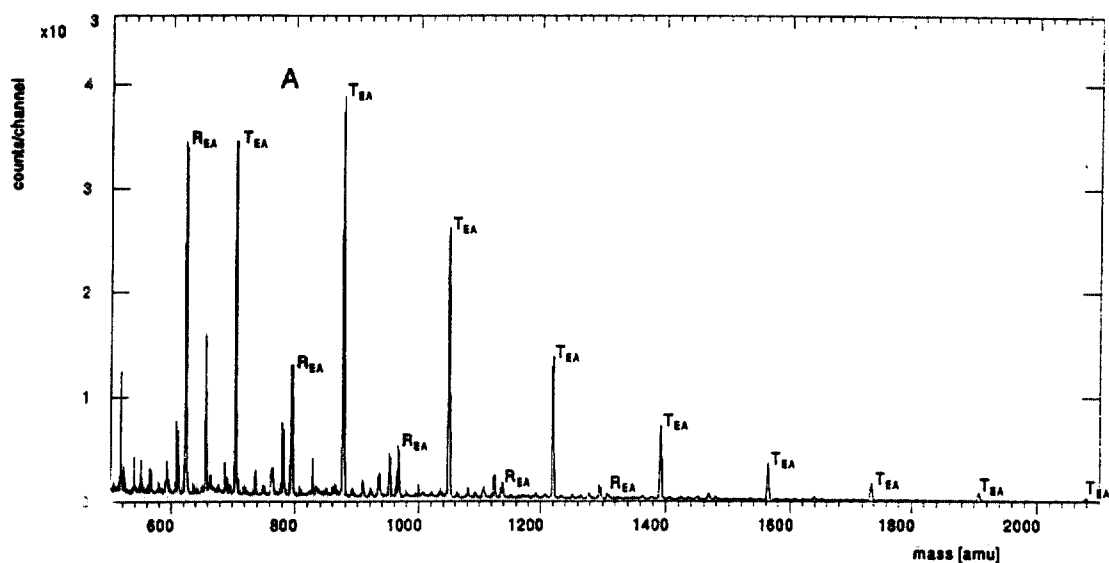


Fig. 2 Positive-ion TOF-SIMS spectrum of poly(ethylene adipate) in trifluoroacetic acid in the mass range $m/z = 500-2100$.

Table I. Main Peaks and Relative Intensities of Poly(butylene adipate) for Different Reaction Time with CF_3COOH .

Peak (m/z)	0.25 hrs	1 hrs	3 hrs	8 hrs
<i>Na Cationized Ion</i>				
$CF_3CO+2R+COCF_3 + Na$ (705) ^a	0.157853	0.508520	0.611545	0.507983
$H+2R+O(CH_2)_4OH + Na$ (713)	0.377793	0.041560	0 ^b	0
$4R+Na$ (823)	0.225134	0.095173	0.054834	0.083720
$CF_3CO+3R+COCF_3 + Na$ (905)	0.092461	0.346257	0.333621	0.408297
$H+3R+O(CH_2)_4OH + Na$ (913)	0.146758	8.49017E-03	0	0
<i>Ag Cationized Ion</i>				
$3R+Ag$ (707)	0.358848	0.121882	0.093351	0.094632
$CF_3CO+2R+COCF_3 + Ag$ (789)	0.126772	0.552899	0.603329	0.542686
$H+2R+O(CH_2)_4OH + Ag$ (797)	0.215969	3.00690E-03	0	0
$4R+Ag$ (907)	0.145321	0.044774	0.028586	0.042686
$CF_3CO+3R+COCF_3 + Ag$ (989)	0.085836	0.275914	0.274734	0.319996
$H+3R+O(CH_2)_4OH + Ag$ (997)	0.067254	1.52404E-03	0	0

a. R = repeat unit.

b. at noise level.

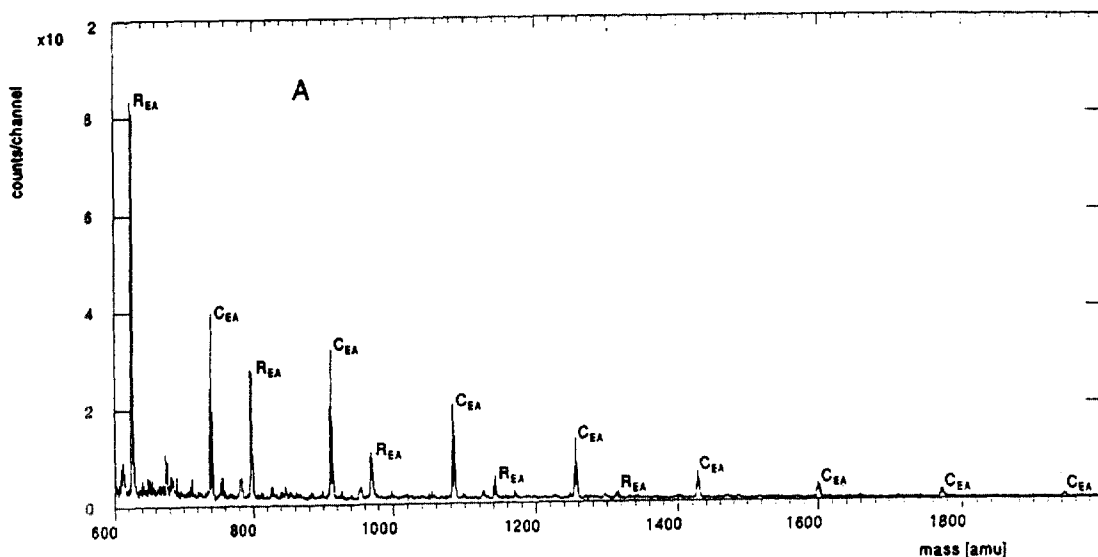


Fig. 3 Positive-ion TOF-SIMS spectrum of poly(ethylene adipate) in chlorodifluoroacetic acid in the mass range $m/z = 600-2000$.

repeat unit peaks of poly(ethylene adipate) are labeled R_{EA} . Peaks of the oligomer for poly(ethylene adipate) are not seen in the spectrum after the reaction. This indicates that all oligomers are reacted at the ester bond. The C_{EA} ions arise from diesters of diol and CFA. They correspond to an integral number of polyester repeat units plus an additional ethanediol and two chlorodifluoroacetates at the diol ends. The mass difference between consecutive C_{EA} peaks with the same cation represents the mass of repeat units of poly(ethylene adipate). For example, in the C_{EA} series of poly(ethylene adipate) for $M=Ag$, the mass difference between peaks for $n=3$ at $m/z = 909$ and $n=4$ at $m/z = 1081$ is equal to $\Delta m/z = 172$, the mass of the repeat unit of poly(ethylene adipate).

Transesterification of polyesters was also carried out in CFA for several different reaction times. The progress of transesterification of poly(ethylene adipate) was monitored at 15 minutes, 1, 3, and 11

hours. The oligomer series peaks are still found in the spectra taken immediately and after 3 hours. The spectrum for the 11 hour reaction does not have the oligomer peaks. The relative intensities of chlorodifluoroacetate ions increase after 3 hours of reaction. This indicates that TOF-SIMS can potentially monitor the progress of such a reaction. The quantitative analysis needs to be investigated further.

4. Conclusions

High resolution Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is a powerful technique for structural characterization of polyesters. TOF-SIMS spectra of a series of polyesters with different diols and diacids were obtained in the mass range $m/z = 0-3500$. Intact oligomers and fragments consisting of a large number of repeat units, were observed. The

mass of the ester repeat unit is determined from spacings between consecutive oligomer and/or fragment peaks.

Transesterification of polyesters by trifluoroacetic acid (TFA) and chlorodifluoroacetic acid (CFA) was studied using the TOF-SIMS. Diesters were produced by transesterification giving a large number of peaks for polyester repeat units with an additional diol and two trifluoroacetates or chlorodifluoro acetates. TOF-SIMS spectra were used to obtain information about the progress of the transesterification reaction. Increasing abundance of tagged ions indicates that the reaction has progressed with time.

This study shows that TOF-SIMS combined with specific reaction is a potentially powerful technique for the characterization of highly branched or cross-linked copolymers.

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