Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Thermal Degradation of Copolymers of N-Vinylcarbazole with Acrylic and Methacrylic Monomers

E. Bilbao[a]; M. Laza[b]; J. L. Vilas[b]; M. T. Garay[b]; M. Rodríguez[b]; L. M. León[b]
[a] Departamento de Ingeniería Química y Medio Ambiente, Escuela Universitaria de Ingeniería Técnica Minera, Universidad del País Vasco (UPV/EHU), [b] Departamento de Química-Física, Facultad de Ciencia y Tecnología, Universidad del Pais Vasco (UPV/EHU), Bilbao, Spain

To cite this Article Bilbao, E. , Laza, M. , Vilas, J. L. , Garay, M. T. , Rodríguez, M. and León, L. M.(2006) 'Thermal Degradation of Copolymers of N-Vinylcarbazole with Acrylic and Methacrylic Monomers', Journal of Macromolecular Science, Part A, 43: 7, 1029 — 1041

To link to this Article: DOI: 10.1080/10601320600740173

URL: http://dx.doi.org/10.1080/10601320600740173

Journal of Macromolecular Science®, *Part A: Pure and Applied Chemistry*, 43:1029–1041, 2006

ISSN 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320600740173

Thermal Degradation of Copolymers of N-Vinylcarbazole with Acrylic and Methacrylic Monomers

E. BILBAO,[2] M. LAZA,[1] J. L. VILAS,[1] M. T. GARAY,[1]
M. RODRÍGUEZ,[1] AND L. M. LEÓN[1]

[1]Departamento de Química-Física, Facultad de Ciencia y Tecnología,
Universidad del Pais Vasco (UPV/EHU), Bilbao, Spain
[2]Departamento de Ingeniería Química y Medio Ambiente, Escuela Universitaria
de Ingeniería Técnica Minera, Universidad del País Vasco (UPV/EHU)

The thermal stability of several series of N-vinylcarbazole and a methacrylic or acrylic monomer has been studied. The copolymers are more stable the higher the content of N-vinylcarbazole, a few units of this monomer being capable of appreciably enhancing the thermal stability of the acrylic or methacrylic homopolymer. The degradation products have been analyzed by FTIR, and a degradation mechanism similar to that for the homopolymers has been proposed. The kinetic analysis based on a differential theoretical model, has allowed an estimate of the activation energy of the degradation process.

Keywords thermal stability, copolymers, N-vinylcarbazole, degradation

Introduction

Poly(N-vinylcarbazole)(PNVC) is a polymer with interesting properties (1–5), but its high glass transition temperature ($T_g = 486\,K$) makes the use of high processing temperatures necessary. The copolymerization of N-vinylcarbazole with several acrylic and methacrylic comonomers allows us to obtain copolymers with NVC units and a T_g lower than PNVC (6, 7). However, potential use of these materials requires the study of their thermal stability, as well as the mechanisms of their thermal degradation for which it is necessary to know the degradation products.

In this work, the thermal stability of different copolymers as a function of their composition, as well as that of the homopolymers, is studied. The analysis of the evolved volatile products and a kinetic study of the degradation process have been carried out.

Received December 2005; Accepted January 2006.

Address correspondence to L. M. León, Departamento de Química-Física, Facultad de Ciencia y Tecnología, Universidad del Pais Vasco (UPV/EHU), Apdo 644, 48080-Bilbao, Spain. E-mail: luismanuel.leon@ehu.es

Experimental

Copolymers of N-vinylcarbazole (NVC) with methyl acrylate (MA), butyl acrylate (BuA), methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BuMA) and cyclohexyl methacrylate (CHMA) have been studied.

The copolymerization reactions were carried out in a thermostatic bath at 323 K, using AIBN as initiator (0.1% by mole with respect to the total amount of monomers) and tetrahydrofuran (THF) as solvent. In all cases, the copolymerization study was extended to cover the entire range of comonomer feed compositions. The required amount of reagents was introduced in the reaction flask, which was evacuated by several freeze-thaw cycles and then sealed under vacuum and placed in the thermostatic bath. Copolymers were precipitated into methanol, redissolved in THF, and reprecipitated in hot methanol for complete elimination of residual NVC monomer. Finally, the copolymers were vacuum dried at room temperature.

The composition of the copolymers was calculated from their nitrogen content determined by elemental analysis; molecular weight was determined (relative to polystyrene standards) by Gel Permeation Chromatography (GPC). According to the results previously reported (6, 7), the copolymers revealed some tendency to alternating, as is further evident in the acrylate series, and when increasing NVC content in the feed composition.

Thermal stability was determined using a Perkin-Elmer Thermobalance TGS-2, following a standard dynamic procedure from room temperature to 873 K at a heating rate of 10 K·min^{-1}. Samples of 6-7 mg and a stream of dry nitrogen (50 ml min^{-1}) were used.

The analysis of the degradation products was carried out by means of a FTIR Spectrophotometer, Nicolet Nexus, connected through an interface to a Shimadzu Thermobalance DTG-60. Samples were run at a heating rate of 5 K·min^{-1} under nitrogen atmosphere (50 ml min^{-1}).

Results and Discussion

The thermal study results of the above copolymer series and the corresponding homopolymers are shown in Tables 1, 2, and 3 where the copolymer composition in NVC mol% (F_1) and the initial degradation temperature (T_i), determined as the intersection between tangents to the baseline and the inflexion point in the thermogram, are listed.

Table 1
Copolymers of N-vinylcarbazole and acrylic comonomer

NVC-MA				NVC-BuA			
Sample	F_1	Ti(K)	Ea (kJ/mol)	Sample	F_1	Ti(K)	Ea (kJ/mol)
PMA	0	636	179	PBuA	0	599	97.0
MA4	11.1	648	267	BuA.2	12.1	635	152
MA5	31.6	660	291	BuA.3	21.6	638	164
MA1	36.0	658	304	BuA.5	31.3	644	172
MA3	48.4	680	298	BuA.8	37.3	651	181
PNVC	100	705	123	BuA.9	38.5	652	186
				BuA.12	46.4	657	200

Table 2

Copolymers of N-vinylcarbazole and methacrylic comonomer

NVC-MMA				NVC-EMA				NVC-BuMA			
Sample	F_1	Ti(K)	Ea (kJ/mol)	Sample	F_1	Ti(K)	Ea (kJ/mol)	Sample	F_1	Ti(K)	Ea (kJ/mol)
PMMA	0	585	211	PEMA	0	531	112	PBuMA	0	512	157
MMA7	4.08	621	319	EMA1	3.67	603	227	BuMA2	3.39	567	173
MMA8	8.31	624	354	EMA2	7.72	607	242	BuMA3	9.22	579	199
MMA1	23.0	646	554	EMA3	19.9	622	258	BuMA5	22.7	606	204
MMA3	40.8	681	480	EMA4	29.0	632	301	BuMA8	39.0	616	212
MMA4	53.5	697	586	EMA5	36.3	646	316	BuMA10	64.5	646	228
PNVC	100	705	123	EMA7	54.5	666	367	PNVC	100	705	123
				PNVC	100	705	123				

Table 3
N-vinylcarbazole/Cyclohexylmethacrylate copolymers

Sample	F_1	Step 1 Ti(K)	Step 1 wt% mass loss	Step 1 Ea (kJ/mol)	Step 2 Ti(K)	Step 2 Ea (kJ/mol)
CHMA.2	9.36	563	65.0	249	663	516
CHMA.5	19.5	573	50.0	320	668	432
CHMA.9	36.4	579	30.8	384	677	354
CHMA.12	47.3	583	34.1	385	674	299
CHMA.8	82.5	578	11.0	279	670	223

In all cases, the thermogravimetric curves indicated that the copolymers degrade at higher temperatures as the NVC content in the copolymer increases as can be seen in Figures 1, 2, and 3 and in Tables 1–3. In some cases, a few units of NVC in the chain are enough to highly improve the thermal stability of the copolymer with respect to the corresponding methacrylic or acrylic homopolymer.

Figure 1 shows the thermogram of PNVC, the common comonomer; the degradation process occurs through only one step until total conversion. Analysis by FTIR of the degradation products revealed that only the monomer (NVC) was produced indicating that the degradation takes place by a depolymerization process, as previously described (8).

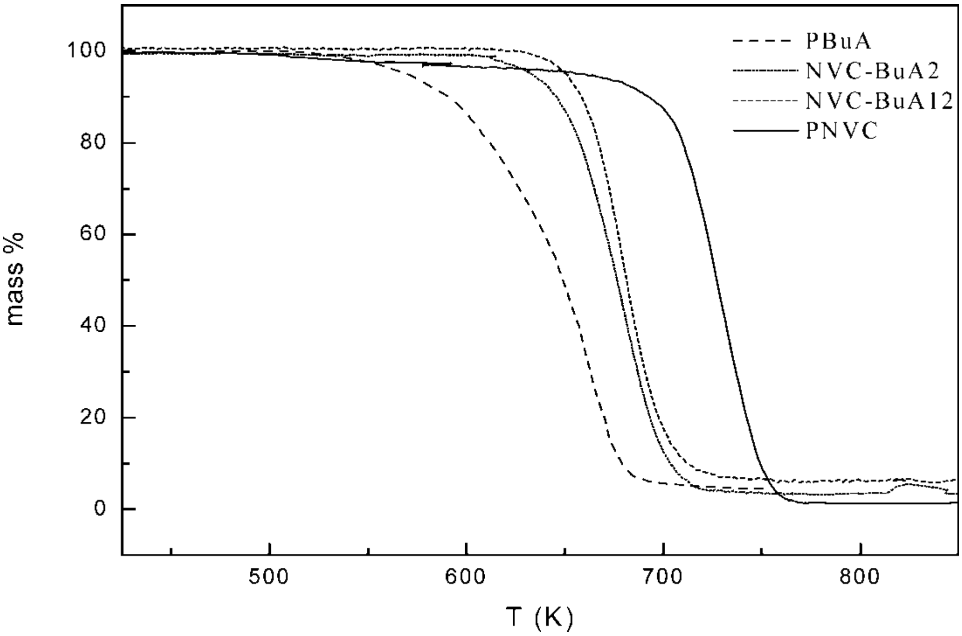


Figure 1. Degradation curves for PNVC, PBuA and NVC-BuA copolymers.

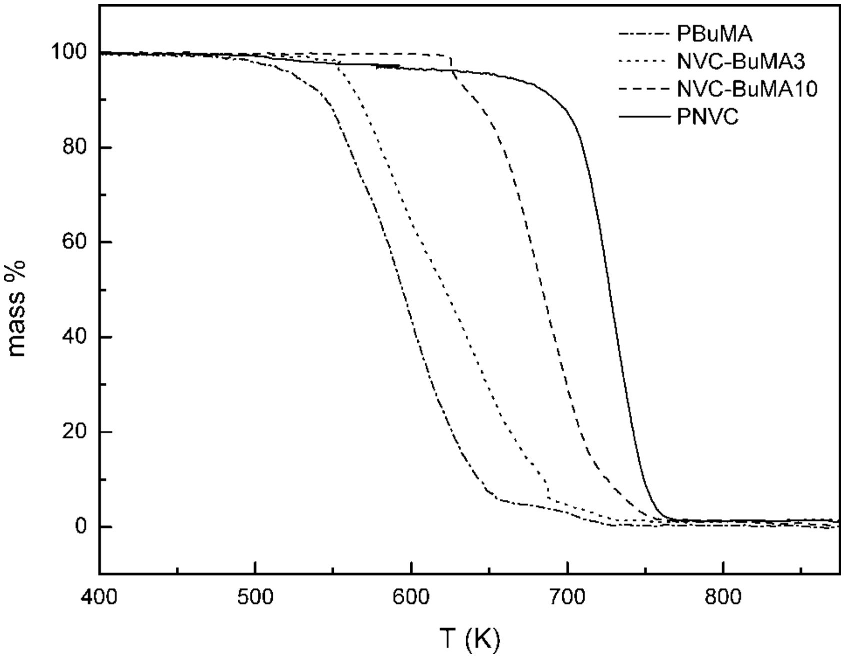


Figure 2. Degradation curves for NVC-BuMA copolymers and homopolymers.

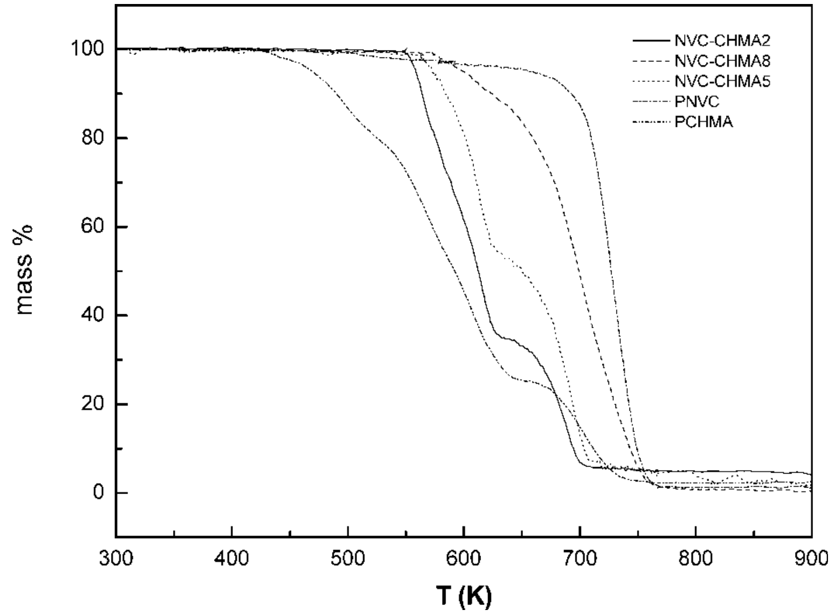


Figure 3. Degradation curves for NVC-CHMA copolymers and homopolymers.

Acrylic Series

As can be seen in Figure 1, the degradation process in all cases consists of only one step until there is practically total conversion. Similar behavior is observed for NVC-MA copolymers (6). FTIR analysis of the degradation products revealed that CO_2 and methyl alcohol were the major degradation products from the PMA homopolymer, the presence of methane and monomer (methyl acrylate) being detected at the end of the process as well. In the case of the PBuA homopolymer, the major degradation products were CO_2 and 1-butanol, with the presence of butene and monomer (butyl acrylate) being observed as well. These results are in agreement with previously published results (9–11), being attributed to inter- and intra-molecular transfer reactions (12).

Figure 4 shows the FTIR spectra obtained in the degradation of a NVC-BuA copolymer, as well as those for NVC and butyl acrylate. It can be deduced that the degradation mechanism is the same as for the corresponding homopolymers. Similar behavior was observed for NVC-MA copolymers, that is, the degradation mechanism is the same as for the homopolymers.

Methacrylic Series

This series includes copolymers obtained with NVC and a methacrylic comonomer, MMA, EMA, BuMA or CHMA, as well as the corresponding methacrylic homopolymers. In general, the behavior of the methacrylic homopolymers (Figure 5) is different from the acrylic ones, a small first stage being observed in the thermogram at the begining of the degradation process, in which an approximate 20% mass loss occurs. After that, the degradation continues until practically total conversion, except for the PCHMA for which two more stages were observed after the initial one.

The initial stage has been attributed to a degradation process beginning at unsaturated chain ends (more reactive) arising from disproportionation reactions during the radical polymerization (8, 13). In order to verify this point, the degradation of anionic PMMA samples was carried out; as can be seen in Figure 6, where the behavior of different

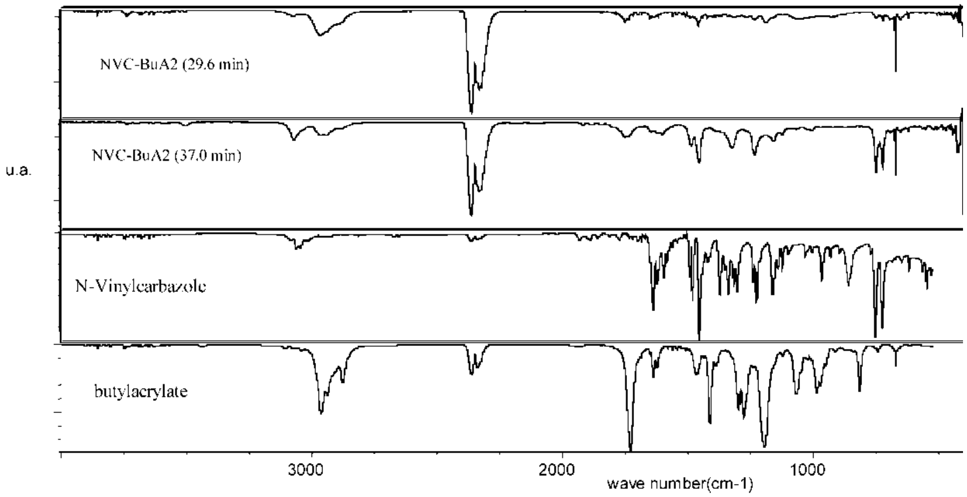


Figure 4. FTIR spectra of degradation products for NVC-BuA copolymers.

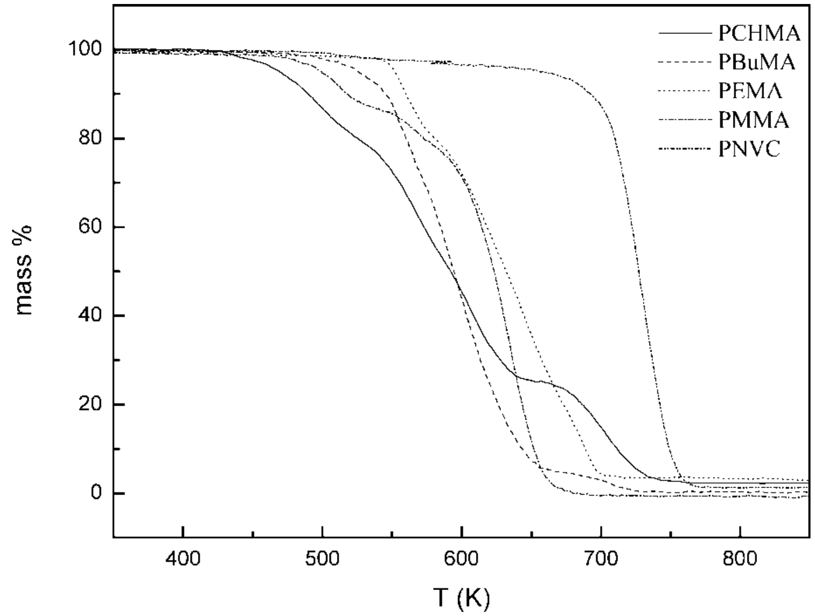


Figure 5. .Degradation curves for methacrylic homopolymers.

radical (RAD1 and RAD2) and anionic (AN1 and AN2) samples are compared, this stage is not observed in the degradation curves of PMMA samples obtained by anionic polymerization (no unsaturated chain ends are present). This stage is not observed in the degradation curves of the corresponding methacrylic copolymers, which can be explained

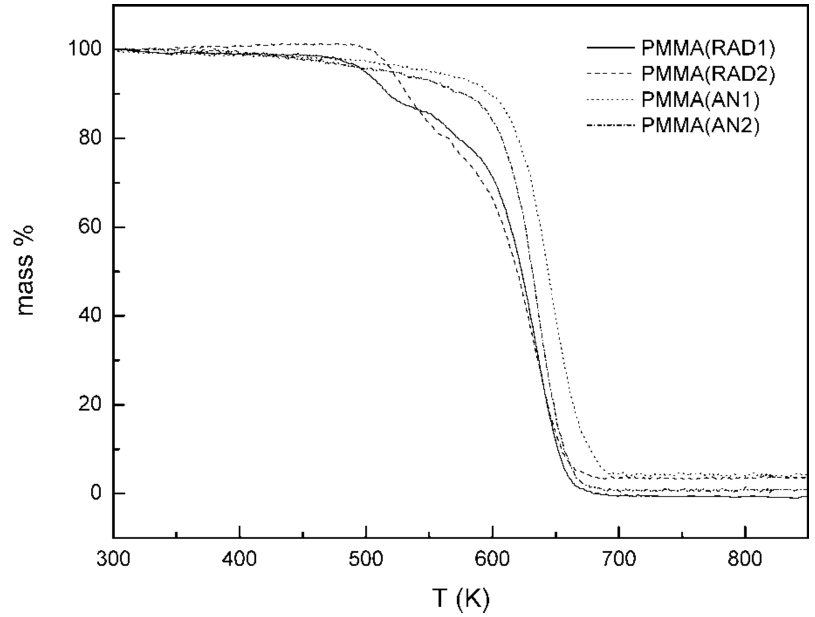


Figure 6. Degradation curves for radical and anionic PMMA.

due to the smaller number of such groups that are present in the copolymers with respect to the homopolymers.

The degradation products from the homopolymers, PMMA, PEMA, and PBuMA, were basically the corresponding methacrylic monomer and, in the case of PEMA, CO_2 and ethene were detected as well. This behavior agrees with that previously described for different polymethacrylates (8, 14).

The degradation of the corresponding copolymers, NVC-MMA, NVC-EMA and NVC-BuMA, yields the same products as the methacrylic and PNVC homopolymers, respectively. The results were the same, independent of the kind of copolymer and their composition. In Figure 7, the FTIR spectra obtained in the case of NVC-BuMA copolymers are presented besides the corresponding to NVC and butyl methacrylate.

From these results, it can be concluded that the main degradation reaction taking place in these methacrylic homopolymers and copolymers is depolymerization initiated by random chain scission reactions, yelding NVC and the methacrylic monomer. The formation of carbon dioxide must obviously be derived from the decomposition of the ester group and it must also produce the corresponding alkene or alkane. The fact that alkene has only been detected in PEMA and NVC-EMA copolymers can be explained considering that the decomposition of the ester groups would be a process which occurs only to a low extent and, moreover, the methane and butene IR bands could be masked by characteristic bands of the monomer.

The behavior of the PCHMA homopolymer and the NVC-CHMA copolymers is somewhat different from the rest of the methacrylic systems. Figure 3 shows the thermograms for several copolymers together with those corresponding to the homopolymers, PNVC and PCHMA.

The degradation process of PCHMA releases cyclohexylmethacrylate, cyclohexene, water and CO_2. The degradation curve of PCHMA has two main stages at $T_i \approx 546\,K$ and $T_i \approx 682\,K$, after the initial stage, with practically a total mass loss being attained at the end. From these results, the following considerations could be made about the degradation mechanism.

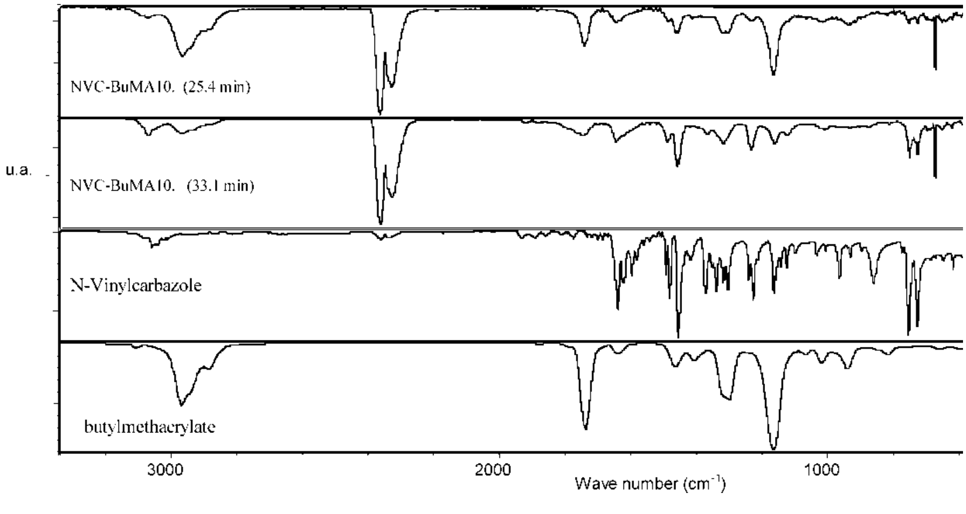


Figure 7. FTIR spectra of degradation products for NVC-BuMA copolymers.

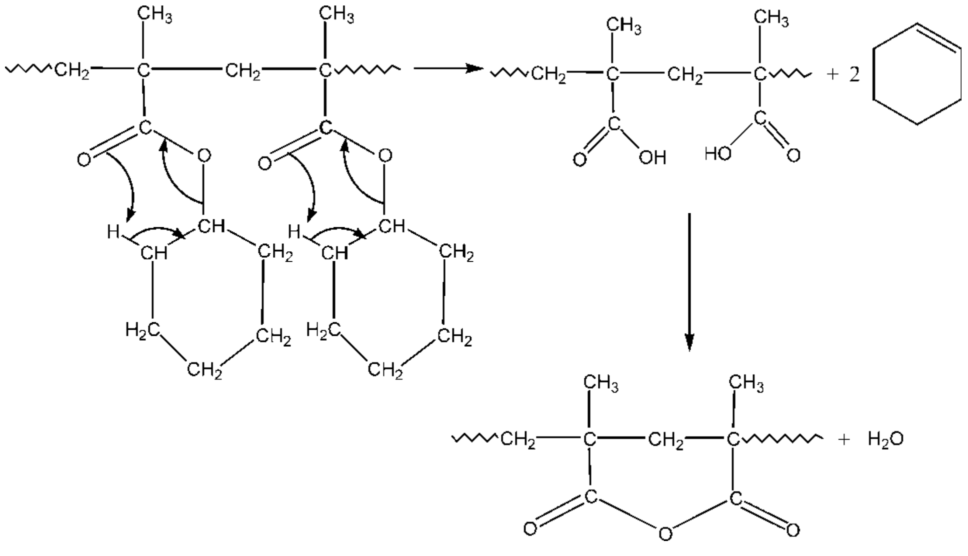
The initial stage (mass loss % < 15) can be attributed to unsaturated chain ends as for other methacrylic polymers. The next stage (considered as the first one) is the most significant with respect to mass loss and begins at a lower temperature than for the rest of the methacrylic homopolymers, indicating that the size of the substituent is a determinant factor on the thermal stability of these polymers. During this stage, the monomer would be produced by a depropagation processes initiated by random chain scission reactions. Cyclohexene would arise from elimination of the lateral substituent and subsequent formation of anhydride (15, 16) as indicated by Scheme 1. During the last stage, the fragmentation of the anhydride structure with the formation of CO_2 would take place.

The thermograms of NVC-CHMA copolymers indicate that the thermal stability is higher as the NVC contents in the copolymer increases, as indicated by the displacement of the thermogravimetric curves towards higher temperatures, that is, NVC units thermally stabilize the polymeric methacrylic chain.

Two steps can be observed in the degradation process of the copolymers as well; as indicated in Table 3, the T_i values for both stages are fairly independent of the copolymer composition; however the relative importance of the two steps depends on it, the first one taking place to a greater extent the lower the contents of NVC. These facts allow us to assume that this step would be related to degradative processes associated with CHMA monomeric units. The degradation products detected by FTIR were the comonomers, NVC and CHMA, CO_2, and cyclohexene as it can be seen in Figure 8. This allows us to conclude that the degradation mechanism is the same as for homopolymers, that is, random chain scission, depropagation and ester group decomposition. For copolymers with lower content of CHMA, however, cyclohexene and CO_2 IR bands were negligible which could be due to the low probability of consecutive CHMA units in the chain.

Kinetic Analysis

This analysis has been carried out for all samples, homopolymers and copolymers.



Scheme 1.

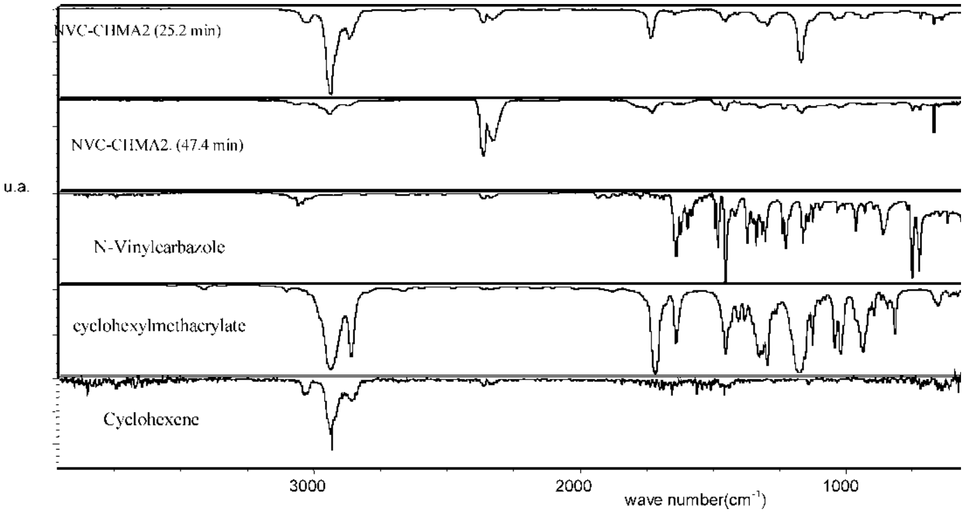


Figure 8. FTIR spectra of degradation products for NVC-CHMA copolymers.

The thermal degradation of a polymeric material can be expressed by:

$$A(solid) \rightarrow B(solid) + C(gas)$$

and its differential rate equation as:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \tag{1}$$

where α is the fraction of A degraded at time t, $k(T)$ is the rate constant and $f(\alpha)$ is a function of the conversion. Assuming for k an Arrhenius relationship with temperature and taking into account that the experiments were carried out at a constant heating rate (β), equation (1) becomes:

$$\frac{d\alpha}{dT} = \frac{\mathrm{Z}}{\beta} \cdot \exp\left(-\frac{E_{\mathrm{a}}}{\mathrm{RT}}\right) \cdot f(\alpha) \tag{2}$$

or in its linear expression:

$$\ln\left[\frac{d\alpha/dT}{f(\alpha)}\right] = \ln\left(\frac{Z}{\beta}\right) - \frac{E_a}{RT} \tag{3}$$

where E_a and Z are the activation energy and the pre-exponential factor, respectively.

To avoid using the integral methods (17), which involves the use of some approximations, we have approached equation (2) by applying the method of Dollimore et al. (18–20) to obtain a function $f(\alpha)$ from some characteristics of the degradation curve, such as the sharp or smooth character of the line at the initial and final degradation temperatures, and the conversion value reached at the temperature for which the degradation rate is maximum.

This method was applied to the homopolymers and the following $f(\alpha)$ functions have been selected:

$$\text{PNVC:} \quad f(\alpha) \equiv \mathrm{B1} = \alpha(1-\alpha)$$

which corresponds to a sigmoidal α-t behavior.

$$\text{Methacrylic homopolymers}: \quad f(\alpha) \equiv \mathrm{D3} = \frac{3}{2}\frac{\sqrt[3]{(1-\alpha)^2}}{1-\sqrt[3]{1-\alpha}}$$

corresponding to a diffusion based mechanism.

$$\begin{aligned} \text{Acrylic homopolmers:} \quad & \mathrm{MA} \quad f(\alpha) \equiv \mathrm{G2} = (1-\alpha)^2 \\ & \mathrm{BuA} \quad f(\alpha) \equiv \mathrm{G1} = 1-\alpha \end{aligned}$$

corresponding to a reaction order based mechanism.

In the cases where more than one function could be adequate, that was selected for which a better fit of experimental results were obtained.

For the different series of copolymers studied, it was observed that the functions corresponding to the homopolymers were not adequate except for samples with a high content of each comonomer. However, in all cases, a linear combination of the $f(\alpha)$ for both involved comonomers gave better fitting results:

$$f_{12}(\alpha) = F_1 \cdot f_1(\alpha) + F_2 \cdot f_2(\alpha)$$

where F_1 and F_2 are the mole fraction of the homopolymers 1 and 2, respectively, and $f_i(\alpha)$ is the function assigned to each homopolymer.

In the case of PCHMA and its copolymers, for which two stages appear in the degradation curves, the $f(\alpha)$ functions were normalized for each stage.

Since the $f(\alpha)$ functions were selected, the values of E_a were obtained from equation (3), and Tables 1–3 show the values for all copolymers.

From the proposed function $f(\alpha)$ and the values of E_a and Z, the theoretical curves were obtained. Figure 9 shows a comparison between the experimental and theoretical

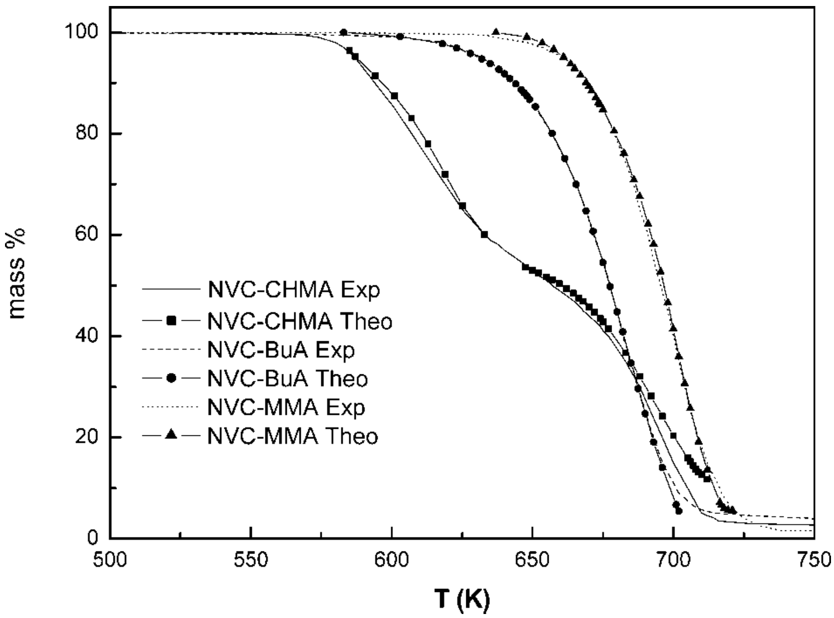


Figure 9. Comparison between experimental and theoretical curve.

curves for some copolymers; as can be seen, there is a good concordance. A similar agreement was obtained for all copolymers.

Conclusions

The copolymers studied, based on NVC and an acrylic or methacrylic comonomer, have a high thermal stability, increasing as the content in NVC increases. On the other hand, as the size of the ester alkyl group increases, the interaction with the polymeric chain is favored with the degradation taking place at a lower temperature. This behavior was observed both in the homopolymers and in the copolymers.

The degradation mechanisms of the copolymers are the same as for the involved homopolymers; that is:

-copolymers of acrylic comonomer degrade by ester group decomposition and intramolecular cyclation processes generating a mixture of CO_2, alcohol and alkene. NVC is also obtained by depolymerization.
-copolymers of methacrylic comonomer degrade by depolymerization, giving the methacrylic monomer and NVC. When the comonomer is CHMA, ester group decomposition takes place as well.

The kinetics of the degradation processes of the copolymers can be described by a differential theoretical model, which assumes the additivity of the functions that reflect the degradation mechanism of the corresponding homopolymers.

Acknowledgements

Authors would like to thank to the Basque Government for finnancial support (Actimat consortium).

References

1. Bloor, D. (1989) Electrical conductivity. In *Comprehensive Polymer Science*; Allen, G. and Bevington, J.C. (eds.); Pergamon Press: Oxford; Vol. 2, 687–705.
2. Grazulevicius, J.V., Strohriegl, P., Pielichowski, J., and Pielichowski, K. (2003) *Progress in Polymer Science*, 28: 1297–1353.
3. Wang, S., Yang, S., Yang, Ch., Li, Z., Wang, J., and Ge, W. (2000) *Journal of Physical Chemistry B*, 104 (50): 11853–11858.
4. Wang, G., Qian, S., Xu, J., Wang, W., Liu, X., Lu, X., and Li, F. (2000) *Physica B*, 279: 116–119.
5. Safoula, G., Napo, K., Bernède, J.C., Touihri, S., and Alimi, K. (2001) *European Polymer Journal*, 37 (4): 843–849.
6. Isusi, M., Rodríguez, M., Garay, T., Vilas, J.L., and León, L.M. (2002) *Journal of Macromolecular Science-Physics*, B41 (2): 241–253.
7. Isusi, M., Rodríguez, M., López, I., and León, L.M. (1997) *Polymer Journal*, 29: 843–847.
8. McNeill, I.C. (1989) Thermal degradation. In *Comprehensive Polymer Science*; Allen, G. and Bevington, J.C. (eds.); Pergamon Press: Oxford; Vol. 6, 451–500.
9. Grassie, N. (1972) *Pure and Applied Chemistry*, 30 (1–2): 119–134.
10. Li, J., Xu, H., Shi, J., Li, Ch., and Bao, Ch. (1999) *Analytica Chimica Acta*, 402: 311–318.
11. Bertini, F., Audisio, G., and Vjacheslav, V.Z. (2005) *Polymer Degradation and Stability*, 89: 233–239.
12. Lehrle, R.S. and Place, E.J. (1997) *Polymer Degradation and Stability*, 56 (2): 221–226.

13. Hu, Y.-H. and Chen, C.-Y. (2003) *Polymer Degradation and Stability*, 82: 81–88.
14. Demirelli, K., Çoskun, M.F., Kaya, E., and Çoskun, M. (2002) *Polymer Degradation and Stability*, 78: 333–339.
15. Bang-Chein, H., Yu-Der, L., and Wei-Kuo, Ch. (1992) *Journal of Polymer Science, Part A: Polymer Chemistry*, 30: 2389–2397.
16. Çoskun, M., Erten, H., Demirelli, K., and Ahmedzade, M. (2000) *Polymer Degradation and Stability*, 69: 245–249.
17. Lyon, R.E. (1997) *Thermochimica Acta*, 297 (1–2): 117–124.
18. Gao, X., Chen, D., and Dollimore, D. (1993) *Thermochimica Acta*, 223 (1–2): 75–82.
19. Dollimore, D., Tong, P., and Alexander, K.S. (1996) *Thermochimica Acta*, 282/283: 13–27.
20. Menon, D., El-Ries, M., Alexander, K.S., Riga, A., and Dollimore, D. (2002) *Instrumentation Science and Technology*, 30 (3): 329–340.