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

Preparation, Degradation, Cyclopentadienylation, and Grafting of PVC's Containing Relatively High Levels of Allylic Chlorines

Béla Iván[a][b]; Joseph P. Kennedy[a]; Tibor Kelen[b]; Ferenc Tüdös[b]
[a] The University of Akron Institute of Polymer Science, Akron, Ohio [b] Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest, Hungary

To cite this Article Iván, Béla , Kennedy, Joseph P. , Kelen, Tibor and Tüdös, Ferenc(1982) 'Preparation, Degradation, Cyclopentadienylation, and Grafting of PVC's Containing Relatively High Levels of Allylic Chlorines', Journal of Macromolecular Science, Part A, 17: 6, 1033 — 1043

To link to this Article: DOI: 10.1080/00222338208056500

URL: http://dx.doi.org/10.1080/00222338208056500

J. MACROMOL. SCI.–CHEM., A17(6), pp. 1033-1043 (1982)

Preparation, Degradation, Cyclopentadienylation, and Grafting of PVC's Containing Relatively High Levels of Allylic Chlorines

BÉLA IVÁN* and JOSEPH P. KENNEDY

The University of Akron
Institute of Polymer Science
Akron, Ohio 44325

TIBOR KELEN and FERENC TÜDŐS

Central Research Institute for Chemistry of the
Hungarian Academy of Sciences
H-1525 Budapest
Hungary

ABSTRACT

Easily modifiable colorless PVC's containing relatively high levels of short internal polyene sequences and allylic chlorines, PVC(A)'s, have been prepared by controlled chemical dehydrochlorination. The thermal and thermooxidative stability of PVC(A)'s decreases significantly in comparison to the original resin. The initial dehydrochlorination rate of PVC(A)'s has been found to be linear with allylic chlorine concentration. Results indicate that nonallylic irregularities, chain-end defect sites, and/or initiation of HCl zip-elimination at regular repeat

---

*Visiting scientist. Permanent address: Central Research Institute for Chemistry of the Hungarian Academy of Sciences, H-1525 Budapest, Hungary.

units may also play a nonnegligible role in PVC instability. Treatment of PVC(A)'s with dimethylcyclopentadienylaluminum (Me_2CpAl) led to cyclopentadienylated PVC's (PVC-Cp) which gelled on drying, and the gel could be solubilized by treatment with strong dienophiles. This indicates Diels-Alder addition between cyclopentadienyl groups and/or polyene sequences of PVC(A). The PVC(A)/BCl_3/i-C_4H_8 system provided efficient grafting of isobutylene and resulted in poly(vinyl chloride-g-isobutylene) in which polyisobutylene branches carry tertiary chlorine termini. The latter could in turn be cyclopentadienylated by treatment with Me_2CpAl and led to networks which could be broken by strong dienophiles.

INTRODUCTION

During the past decade many interesting cationic derivatizations leading to unique novel materials have been carried out [1, 2, 7]. In the course of these studies, carbocationic techniques proved to be eminently suitable for modification of PVC [1, 3-6], and it has been determined that the chemical transformations take place only at labile (tertiary and/or allylic) chlorine sites. The secondary chlorine containing repeat units in PVC are reluctant to participate in these cationic reactions. Effective derivatizations, e.g., grafting [1, 4] and cyclopentadienylation [5-7], require the presence of a certain minimum concentration of labile chlorines in PVC. For example, the preparation of impact resistant (rubber-toughened) PVC or cyclopentadienylated PVC, giving thermally reversible networks, would require 1-4 labile chlorines per chain in PVC. However, even the lowest quality commercial PVC was found to contain less than this minimum concentration of labile chlorines.

The aim of this research was to obtain colorless PVC's containing relatively high levels of allylic chlorines, PVC(A), by controlled dehydrochlorination and subsequently to study cationic modification, i.e., cyclopentadienylation and grafting, of these resins. Parallel to PVC modification research, thermal and thermooxidative degradation studies on PVC(A)'s have also been carried out. According to experimental evidence using model compounds, allylic chlorines are thermally unstable and may provide the main initiation sites of HCl zip-elimination during PVC degradation [8]. However, very few attempts have been made to investigate degradation of PVC's containing known concentrations of allylic chlorines. Michel and co-workers [9] have recently studied the degradation behavior of vinyl chloride/phenylacetylene copolymers and have found a significant effect of such structures on the stability of the resin.

EXPERIMENTAL

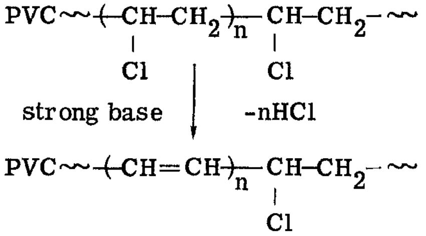
A carefully purified commercial suspension PVC (Geon 103, from B. F. Goodrich) has been used.

Experimental details of chemical dehydrochlorination, purification, thermal and thermooxidative degradation, cyclopentadienylation with dimethylcyclopentadienylaluminum (Me_2CpAl), grafting with isobutylene, and characterization techniques including GPC, UV-visible spectroscopy, and ozonization of PVC's are given elsewhere [5, 6].

RESULTS AND DISCUSSION

Controlled Dehydrochlorination of PVC with Strong Base

The first phase of our work concerned the preparation of colorless PVC's containing relatively high concentrations of allylic chlorines, PVC(A)'s, by controlled chemical dehydrochlorination. A series of experiments [6], i.e., treatment of PVC with t-BuOK in THF solution, under a variety of reaction conditions, yielded PVC's containing increased concentrations of allylic chlorines in the chain (cf. Table 1) at the same time keeping the number of conjugated double bonds equal to or below ~3:



$$\mathrm{PVC}\sim\!\sim\!(\underset{\mathrm{Cl}}{\mathrm{CH}}\!-\!\mathrm{CH_2})_n\!-\!\underset{\mathrm{Cl}}{\mathrm{CH}}\!-\!\mathrm{CH_2}\!-\!\sim\!\sim \xrightarrow[\text{-nHCl}]{\text{strong base}} \mathrm{PVC}\sim\!\sim\!(\mathrm{CH}\!=\!\mathrm{CH})_n\!-\!\underset{\mathrm{Cl}}{\mathrm{CH}}\!-\!\mathrm{CH_2}\!-\!\sim\!\sim$$

where n ≤ 3. The presence of allylic chlorines has been detected by ozonolysis, cadmium acetate treatment combined with FT IR spectroscopy, and phenolysis [14]. These characterization experiments prove the reaction scheme above, and indicate that substitution of allylic chlorines during base treatment of PVC is essentially absent. Similar conclusions have recently also been reported by other workers [15].

Figure 1 shows a representative UV-visible spectrum of a PVC(A). Absorbances are absent in the visible region and appear only below 300 nm, i.e., in a region characteristic for conjugated double bonds with n < 3 [10]. A two-parameter kinetic model was constructed to describe the dehydrochlorination process in semiquantitative terms [6]. Conclusions based on this model are in good agreement with experimental findings.

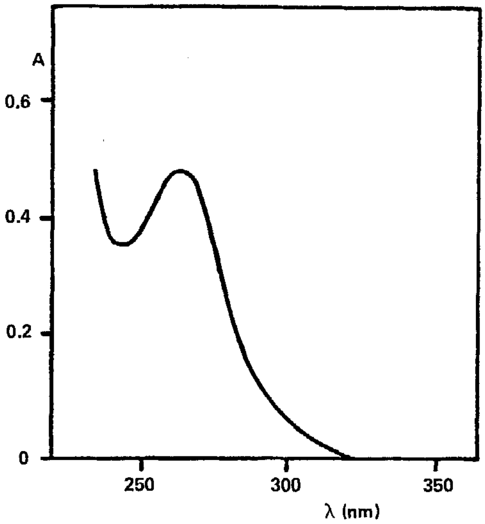


FIG. 1. UV-visible spectrum of a PVC(A) sample obtained by controlled chemical dehydrochlorination.

Base treatment of PVC is known to result in random E2 elimination of HCl from the chain [11] and thus to yield randomly distributed single and/or conjugated double bonds (polyenes). According to the scheme above, both types of unsaturations necessarily produce random allylic chlorine sites.

Thermal and Thermooxidative Degradation of PVC(A)

It is widely accepted that subanalytical concentrations of allylic chlorines in PVC greatly influence heat and oxidative sensitivity of the resin. Thus it was of interest to study the thermal and thermooxidative degradation behavior of PVC(A)'s. Figures 2 and 3 and Table 1 summarize results obtained during thermal degradation (190°C, N_2) of a series of PVC(A)'s. Evidently introduction into PVC of a low concentration of allylic chlorines significantly decreases its thermal stability. According to the data in Fig. 3 and Table 1, the rate of initial dehydrochlorination $(V_{HCl})_0$ is a linear function of the number of internal polyenes, i.e., allylic chlorines, in PVC, the concentration of which (S) has been quantified by ozonolysis. The relatively high intercept in the $(V_{HCl})_0$ versus S plot in Fig. 3 may be an indication that 1) nonallylic irregularities, e.g., tertiary chlorines, are also present in the resin, 2) chain ends possess unstable structures,

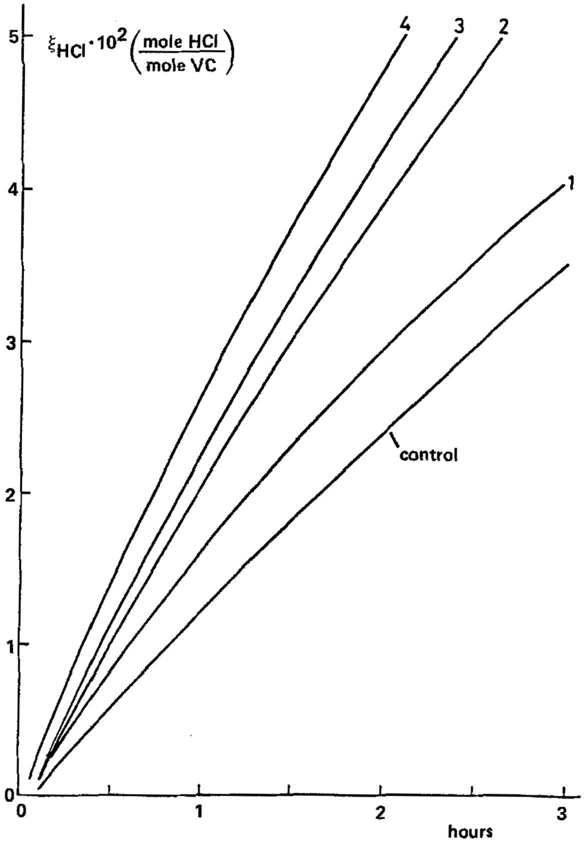


FIG. 2. Extent of HCl loss as a function of time during thermal degradation (190°C, N_2) of PVC(A)'s containing different amount of allylic chlorines (for identification see Table 1).

and/or 3) the rate of initiation of HCl chain elimination on a regular unit of PVC is higher than commonly assumed.

Figure 4 shows the extent of HCl loss (ξ_{HCl}) as a function of time for PVC(A)'s at 180°C under an oxygen atmosphere. Thermooxidative stability decreases significantly by increasing the concentration of internal allylic sites in PVC. According to the "minimal scheme" of the mechanism of thermooxidative PVC degradation [12], this effect may be due to accelerated initiation of dehydrochlorination and fast oxidation of polyenes yielding radicals which may induce HCl loss by attacking regular repeat units in PVC.

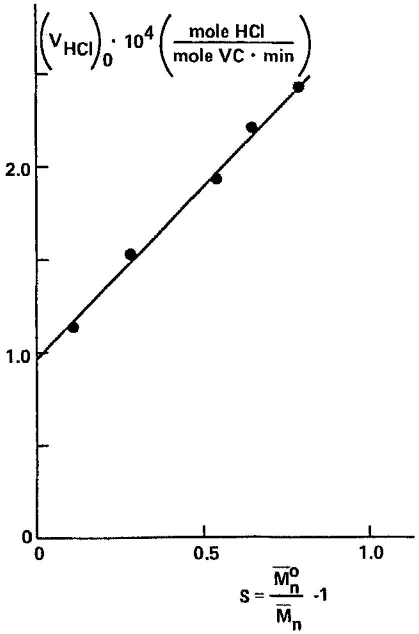


FIG. 3. Initial rate of HCl loss as a function of internal polyene concentration in PVC(A)'s during thermal degradation (190°C, N_2).

Cyclopentadienylation of PVC(A)

PVC(A) samples have been treated with Me_2CpAl in dry CH_2Cl_2 solution under a dry nitrogen atmosphere. On the basis of earlier studies [2, 5, 7], cyclopentadienylation of allylic chlorine containing PVC(A)'s is expected to yield PVC's carrying pendant Cp groups (PVC-Cp). Similarly to some of the other organoaluminums [1-3], Me_2CpAl also substitutes labile, i.e., allylic and/or tertiary, chlorines [7].

Cyclopentadienylated and subsequently vacuum-dried PVC(A)'s gave insoluble networks provided the allylic chlorine concentration of PVC(A) was relatively high. The cyclopentadienylated products, however, could be solubilized by the addition of strong dienophiles, e.g., maleic anhydride and dimethyl acetylene dicarboxylate. The three sets of equations shown on page 1041 illustrate network formation by Diels-Alder addition involving pendant cyclopentadienyl groups in PVC and the fact that these networks are thermally reformable. The addition of strong dienophiles traps the unreacted pendant Cp groups, i.e., permanently prevents their Diels-Alder addition, and thus solubilizes the network.

TABLE 1. Molecular Weight, Internal Allylic Chlorine Concentration $[S = (\overline{M}_n{}^0/\overline{M}_n) - 1]$ Determined by Ozonolysis, and Initial Rate of HCl Loss $(V_{HCl})_0$ during Thermal Degradation (190°C, N_2) of PVC(A)'s

Sample	Before ozonization		After ozonization		$S = \dfrac{\overline{M}_n{}^0}{\overline{M}_n} - 1$	$(V_{HCl})_0 \times 10^4$ (mol HCl/mol VC/min)
	$\overline{M}_n{}^0 \times 10^{-3}$	$\overline{M}_w{}^0/\overline{M}_n{}^0$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$		
Control	64.2	1.77	57.8	1.80	0.11	1.14
1	62.4	1.78	48.7	1.82	0.28	1.53
2	61.9	1.83	40.2	1.81	0.54	1.93
3	65.1	1.80	39.4	1.76	0.65	2.21
4	63.9	1.79	35.7	1.81	0.79	2.43

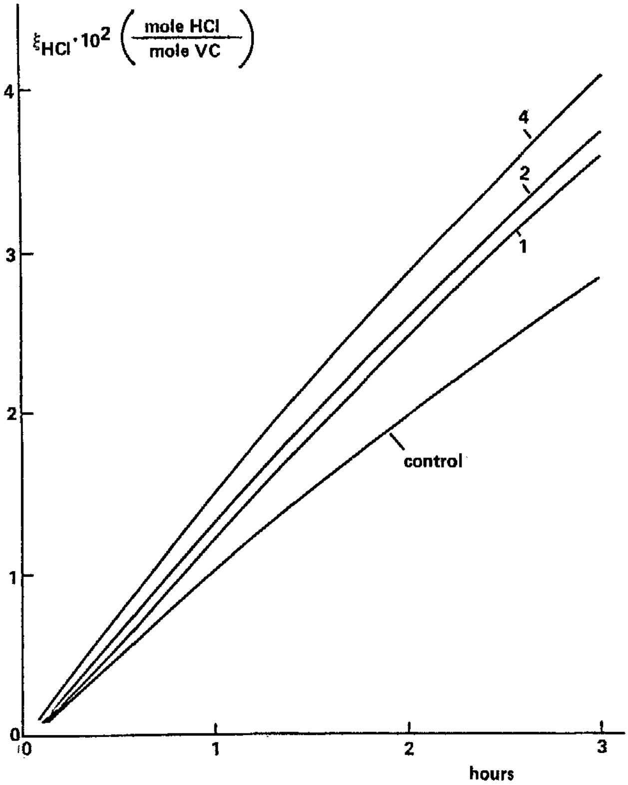
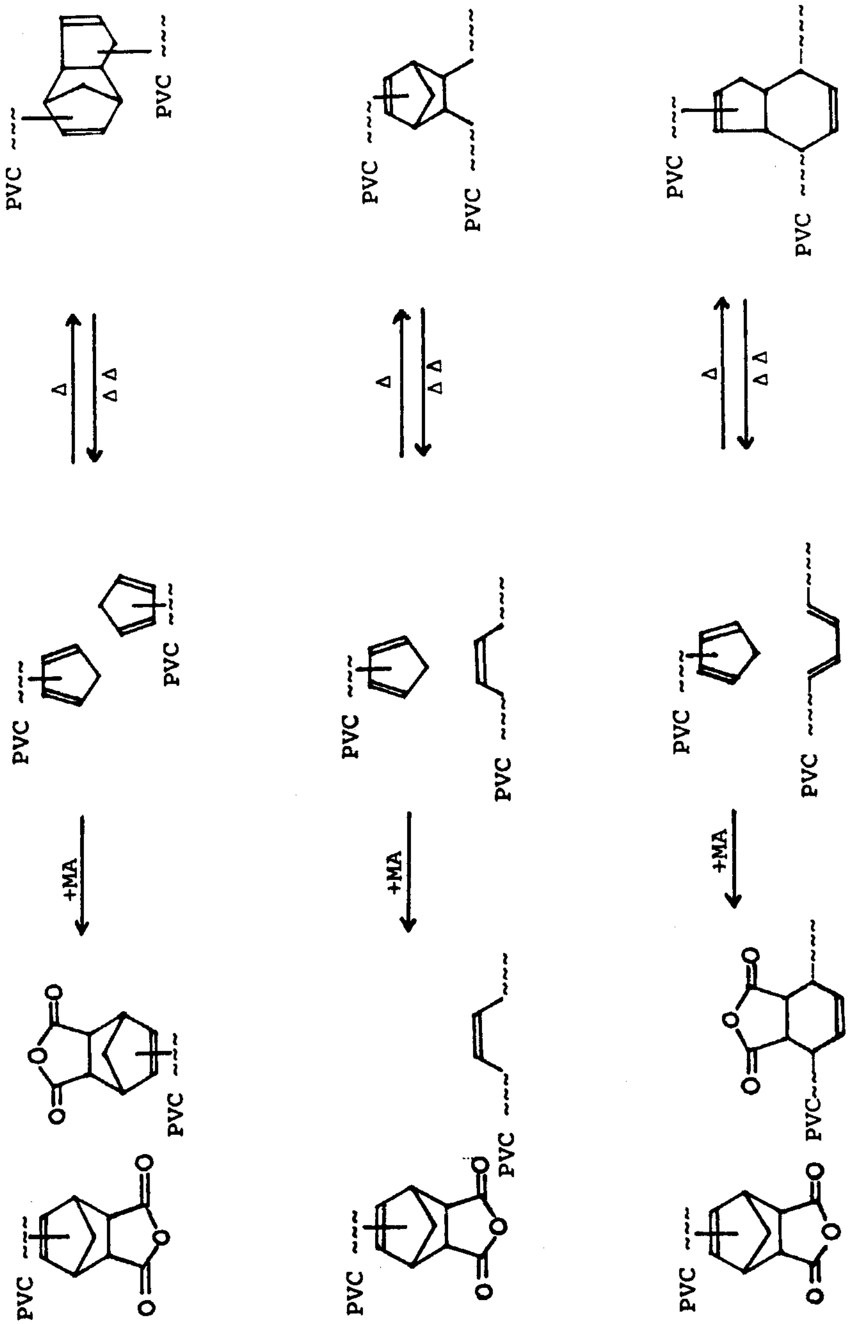


FIG. 4. Extent of HCl loss as a function of time during thermo-oxidative degradation of PVC(A)'s (180°C, O_2).

Synthesis and Cyclopentadienylation of PVC-g-PIB-Cl

Substituted allylic chlorines in conjunction with BCl_3 are efficient initiators of isobutylene polymerization, and the polyisobutylenes thus obtained carry tertiary chlorine termini [4, 13]. Based upon this information, a series of poly(vinyl chloride-g-isobutylenes)-carrying tertiary chlorine termini at the polyisobutylene branches (PVC-g-PIB-Cl) have been prepared using the PVC(A)/BCl_3 graft-initiating system. According to the data in Fig. 5, grafting efficiency (GE) increases with allylic chlorine concentration and approaches ~90%. Previous cationic graftings of PVC's [1] have resulted in relatively low grafting efficiencies, most likely due to the relatively low level of labile chlorines in the resin, i.e., to the fact that the concentration


PVC
Δ
Δ Δ
+MA
O

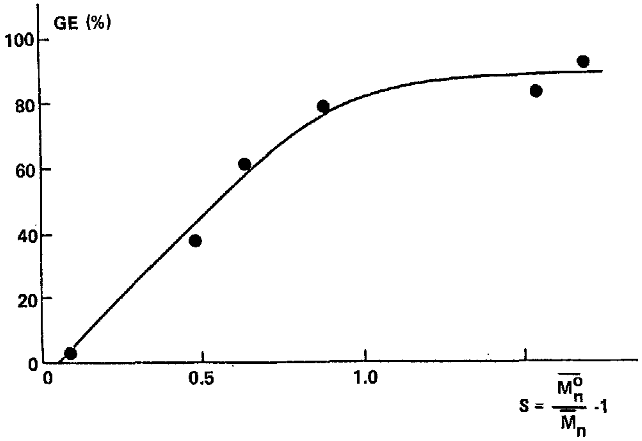


FIG. 5. Grafting efficiency as a function of internal polyene concentration in PVC(A)'s for PVC(A)/BCl_3/i-C_4H_8 systems.

of labile chlorines in PVC and that of cationogenic impurities in the system are commensurate. In the PVC(A)'s used in this research, the allylic chlorine concentration is relatively high and the BCl_3 coinitiated isobutylene polymerization is free from chain transfer to the monomer, which explains the relatively high grafting efficiencies.

The polyisobutylene branches with tertiary chlorine termini have been cyclopentadienylated by treatment with Me_2CpAl. Cyclopentadienylation of PVC-g-PIB-Cl yielded graft copolymers in which the polyisobutylene branches carry the endgroup PVC-g-PIB-Cp. After drying for 2-3 d in the dark under vacuum, these copolymers gave networks which could be solubilized by treatment with high concentrations of strong dienophiles in refluxing THF. Network formation is evidently reversible and may be attributed to Diels-Alder addition of cyclopentadienyl groups.

ACKNOWLEDGMENTS

Financial contributions by the National Science Foundation (INT-78-24275), USA, and the Institute for Cultural Relations, Hungary, are gratefully acknowledged.

REFERENCES

[1] J. P. Kennedy (ed.), *Cationic Graft Copolymerization, Appl. Polym. Symp.*, *30* (1977).

[2] J. P. Kennedy, Makromol. Chem., Suppl., 3, 1 (1979).
[3] K. Mitani, T. Ogata, M. Nakatsukasa, H. Awaya, and Y. Tomari, J. Macromol. Sci.–Chem., A12, 531 (1978).
[4] S. N. Gupta and J. P. Kennedy, Polym. Bull., 1, 253 (1979).
[5] B. Iván, J. P. Kennedy, T. Kelen, and F. Tüdős, Ibid., 1, 415 (1979).
[6] B. Iván, J. P. Kennedy, T. Kelen, and F. Tüdős, J. Polym. Sci., Polym. Chem. Ed., 19, 9 (1981).
[7] J. P. Kennedy and K. F. Castner, Ibid., 17, 2055 (1979).
[8] W. H. Starnes, Jr., Adv. Chem. Ser., 169, 309 (1978).
[9] A. Guyot, M. Bert, P. Burille, M. F. Llauro, and A. Michel, Third Int. Symp. PVC, Cleveland (USA), Prepr., p. 46 (1980).
[10] T. Kelen, G. Bálint, G. Galambos, and F. Tüdős, Eur. Polym. J., 5, 597 (1969).
[11] Y. Shindo and T. Hirai, Makromol. Chem., 155, 1 (1972).
[12] F. Tüdős, T. Kelen, and T. T. Nagy, Dev. Polym. Degradation, 2, 187 (1979).
[13] J. P. Kennedy, S. Y. Huang, and S. C. Feinberg, J. Polym. Sci., Polym. Chem. Ed., 15, 2869 (1977).
[14] B. Iván, F. Tüdős, O. Egyed, and T. Kelen, To Be Published.
[15] A. Perichaud, D. Dussoubs, and L. Savidan: C. R. Acad. Sci., Paris, Sér. C, 290, 65 (1980).