Polymer Bulletin 48, 345-352 (2002)

Polymer Bulletin

Cationic grafting of norbornadiene, indene, and 1,3-cyclohexadiene from PVC

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Received: 8 October 2001/ Revised version: 22 April 2002/ Accepted: 23 April 2002

Summary

The synthesis of three novel graft copolymers consisting of a PVC backbone fitted with polynorbornadiene (PNbd), polyindene (PInd), polycyclohexadiene (PCHD) branches, i.e., PVC-*g*-PNbd, PVC-*g*-PInd, and PVC-*g*-PCHD, is described. The synthesis strategy was to initiate the grafting of norbornadiene (Nbd), indene (Ind), and 1,3-cyclohexadiene (CHD) by a PVC containing ~ 1.6 active (tertary and allylic) chlorines in conjunction with Et_2AlCl. The products were characterized by solvent fractionation, molecular weight determination, T_g, and NMR spectroscopy. The effect of temperature on the grafting was investigated in the 20 to –50 °C range.

Introduction

Conventional commercially available PVC is known to contain tertiary and allylic (“active”) chlorines[1] which in the presence of certain Fridel-Crafts halides (e.g., alkyl aluminums, $SnCl_4$, $TiCl_4$)[2,3] have been shown to mediate the grafting of cationically polymerizable monomers such as isobutylene, styrene, α-methylstyrene[4]. Millán et al. believe that isobutylene can be grafted from PVC in the presence of Et_2AlCl at “active” isotactic triads, however, their ^{13}C NMR evidence is at best circumstantial[5].

The objective of the present research was to extend the scope of this chemistry and to synthesize heretofore unknown graft copolymers containing the PVC backbone fitted with PNBD, PInd, and PCHD branches.

Experimental

Materials. Chemicals were purchased from Aldrich, except as specified. Poly(vinyl chloride) (PVC) (Geon ® Resin 110×377, by The Geon Company, M_n = 36,600 g/mol) was purified according to a published procedure[6]. The number of active chorines of this PVC is ~1.6 per chain[7]. Anhydrous 1,2-dichloroethane (DCE), anhydrous methylene chloride, norbornadiene (Nbd), indene (Ind), 1,3-cyclohexadiene (CHD), and diethylaluminum chloride (1 *M* solution in hexanes) were used as received without further purification.

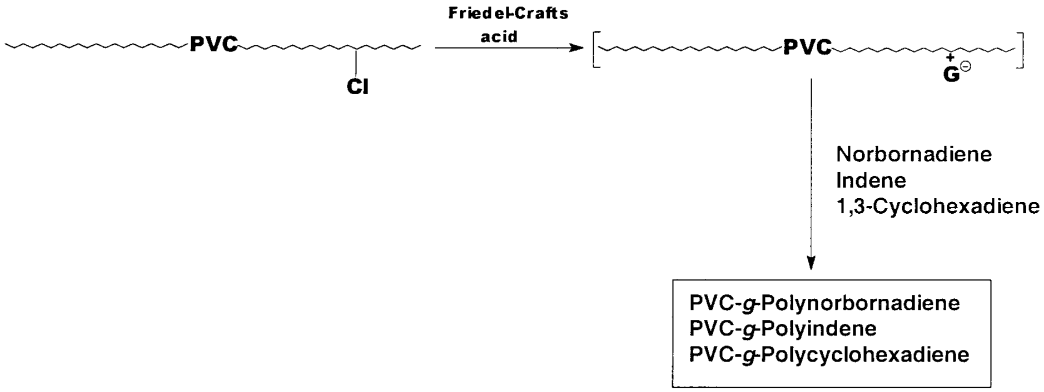
Grafting of Nbd, Ind, and CHD from PVC. Procedures used for the grafting of

Nbd, Ind, CHD from PVC were similar to a published procedure[4]. A representative grafting was carried out as follows: A 500 mL flask, equipped with mechanical stirrer, was charged with 250 mL of a 1 wt % PVC solution in DCE (or methylene chloride if the experiment was carried out at –50 °C) and cooled to the desired temperature. Monomer (Nbd, Ind, CHD = 0.4 mol/L) and diethylaluminum chloride (4.0×10^{-2} mol/L) were added under stirring. After 60 minutes methanol (~10 mL) was added to the charge to terminate the reaction. The charge was moved from the drybox to a hood, precipitated into an excess of methanol, and filtered. The precipitate was extracted with a toluene/hexanes (50/50) mixture to separate the homopolymer from the graft. PNbd, PInd, and PCHD are soluble in this mixture. The homopolymer solution was evaporated under a hood and the product dried in a vacuum oven. The graft was dissolved in THF, the solution centrifuged for 1 hour to remove aluminum oxide residues, the supernatant decanted, the THF removed by evaporating under a hood, and the purified graft dried in a vacuum oven at room temperature. The weights of the graft and the homopolymer were determined gravimetrically.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded by a Varian 300 spectrometer. Molecular weights were determined by a Waters high pressure GPC instrument as described[8]. The molecular weights of grafts were estimated by RI (GPC) since it has been established that the grafting of a maximum of 1.6 branches per PVC does not compromise this analytical method[7]. Grafting-from efficiency (G_{eff}), the extent of grafting (G_{poly}), and the number of branches were determined according to a published method[4]. Glass transition temperatures (T_g) were determined by a published procedure[9].

Results and Discussion

Scheme I outlines the overall synthetic strategy for the preparation of PVC-*g*-PNbd, PVC-*g*-PInd, and PVC-*g*-PCHD:



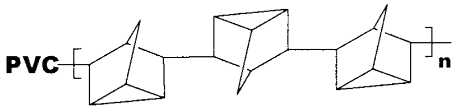
Scheme I. The grafting of Nbd, Ind, and CHD from PVC.

This strategy has already been used for the grafting of IB, St, and β-pinene from PVC by the use of Et_2AlCl[4].

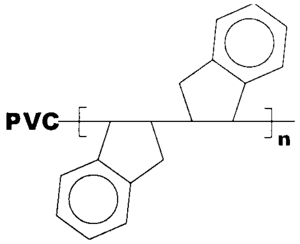
Tables I - III summarize the data. In these experiments the PVC initiator was dissolved in DCE or CH_2Cl_2, monomer (i.e. Nbd, Ind, CHD) was added, and the grafting was initiated by the addition of Et_2AlCl to the charges stirred at a preselected temperature. The homopolymers (PNbd, PInd, PCHD) were separated from the target graft copolymers by solvent extraction. It was assumed that the amount of ungrafted PVC is negligible in the final product and that the grafting of the branches occurred by conventional cationic polymerization with chain transfer to the monomer so that the M_n's of the extracted homopolymers reflected those of the grafted branches. Thus the amount and molecular weight of the homopolymers were determined and the data used to calculate grafting efficiency (G_{eff}), the extent of grafting (G_{poly}) and the number of grafted branches per PVC backbone[4].

A. Grafting of High T_g Branches

The grafting of Nbd and Ind from PVC was undertaken to attach high Tg branches to the backbone: $T_{g,PNbd} = 320$[10] and $T_{g,Ind} = 194$ °C[9]. The high glass transition of PNbd and PInd are due to the very rigid chains of these polymers. The repeat structures of these molecules are illustrated below:



PVC-*g*-PNbd

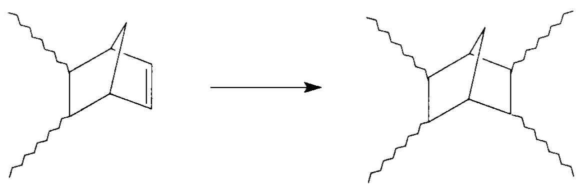


PVC-*g*-PInd

Table I. The effect of temperature on grafting of norbornadiene from PVC

Temp.	G_{eff}	G_{PNbd}	$M_{n,PVC\text{-}g\text{-}PNbd}$	$M_{w,PVC\text{-}g\text{-}PNbd}$	$M_{n,PNbd}$	Number of Branches
°C	%	%		10^{-3} g/mole		
20	18.6	14.3	42.0	81.5	3.8	1.6
-10	24.3	16.3	43.0	85.0	5.4	1.2
-30	39.2	19.7	43.7	89.0	6.1	1.2
-50	63.1	26.0	48.6	94.0	9.2	1.3

Table I shows the effect of temperature on the grafting of Nbd in the 20 to –50 °C range. The G_{eff}, the G_{PNbd}, the $M_{n,PVC\text{-}g\text{-}PNbd}$, and the $M_{n,PNbd}$ increase with decreasing temperature because the rate of chain transfer is decreasing. The number of branches does not change with temperature within what is considered experimental variation suggesting efficient initiation of grafting even at –50 °C. The products, both PVC-*g*-PNbd and PNbd, obtained in the –10 to –50 °C range were soluble in THF. A small amount (~ 5%) of insoluble material was obtained at 20 °C. The origin of this fraction is most likely crosslinking at the higher temperature due to the formation of 2,3-disubstituted repeat units:



The glass transitions of a representative PVC-*g*-PNbd prepared at – 30 °C were determined (see Table I). The DSC trace showed the presence of a low temperature transition at 78.5 °C associated with PVC, and a higher temperature transition at 178.6 °C due to the presence of PNbd branches. The difference between the T_g found in this research and that published earlier[10], is most likely due to the lower M_n of the branch (M_n = 6,100 g/mol) than that of the PNbd studied in ref. 10 (M_n = 9,850 g/mol).

Figure 1 shows the ^{1}H and ^{13}C NMR spectra of PVC-*g*-PNbd. Based on spectroscopic analysis, the 2,6-disubstituted nortricyclic structure in PVC-*g*-PNbd was confirmed.

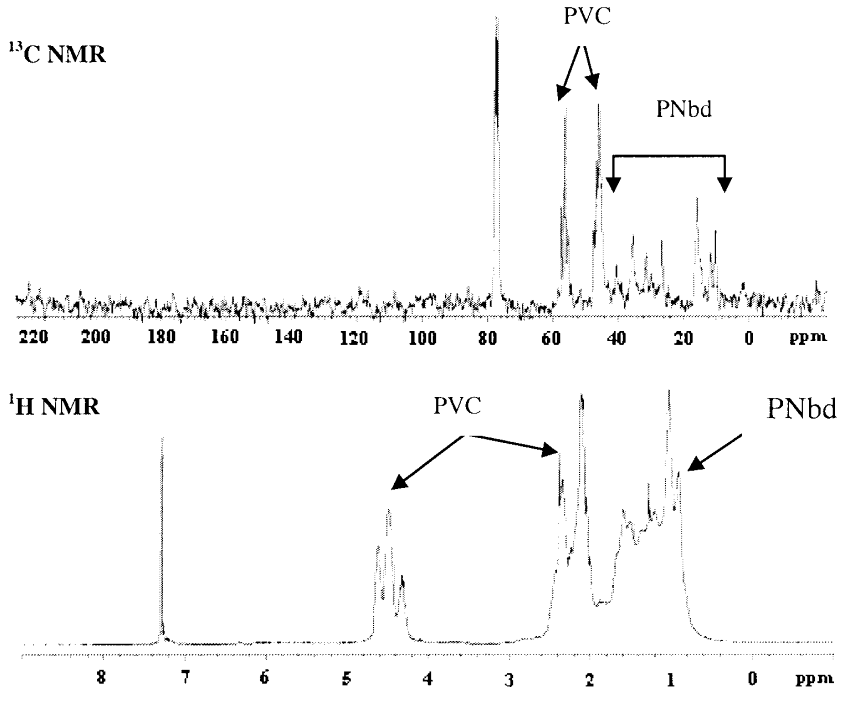


Figure 1. ^{1}H and ^{13}C NMR spectra of PVC-*g*-PNbd.

The results obtained with Ind (Table II) and their interpretation are similar to those obtained with Nbd, namely, decreasing the temperature tends to "freeze out" chain transfer to monomer which leads to an increase of G_{eff} and branch molecular weight. In these experiments all products were soluble in THF. The molecular weights of PInd's obtained were higher by a factor of two than those of PNbd's.

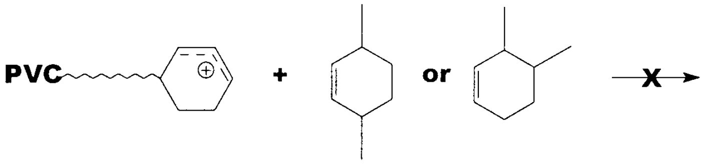
The T_g's of PVC-*g*-PInd with $M_{n,PInd}$ = 9,800 g/mol prepared at – 10 °C (see Table II) were determined. The T_g scan showed two transitions; one at 79.3 °C for PVC and another at 172.5 °C for the PInd branches. The T_g of a PInd with M_n = ~20,000 g/mol was 194 °C[9], most likely because this PInd was of higher molecular weight than that of the branches in PVC-*g*-PInd.

Table II. The effect of temperature on grafting of indene from PVC

Temp.	G_{eff}	G_{PInd}	$M_{n,PVC\text{-}g\text{-}PInd}$	$M_{w,PVC\text{-}g\text{-}PInd}$	$M_{n,PInd}$	Number of Branches
°C	%	%		10^{-3} g/mole		
20	17.2	16.6	43.9	86.4	8.6	0.9
-10	22.3	20.1	46.2	88.2	9.8	1.0
-30	45.7	24.7	48.6	95.5	13.2	1.0

B. Unsaturation by Grafting

The grafting of 1,3-cyclohexadiene from PVC was investigated in order to create branches carrying multiple unsaturations. CHD is readily polymerizable cationically[11] and every repeat unit of the PCHD chain introduces one double bond to the graft. Crosslinking and gelation, however, may occur, thus the experimental challenge was to develop conditions for grafting in the absence of this undesirable side-reaction. Table III shows the data. Gratifyingly, the products were soluble indicating the absence of gelation even at 20 °C. We speculate that gelation did not occur because of the relatively low molecular weight of the PCHD branches and/or high steric compression:



The structure of PCHD branches in the grafts has been characterized by ^{1}H NMR spectroscopy (Figure 2). According to the results, PCHD branches in PVC-*g*-PCHD consist of 1,4 and 1,2 structural units with the 1,4 unit predominating.

Similar to the NBd and Ind systems discussed above, the effect of temperature is clearly discernible also with CHD. According to the data shown in column 7 of Table III, the estimated number of double bonds incorporated in the graft is high and increases with declining temperature.

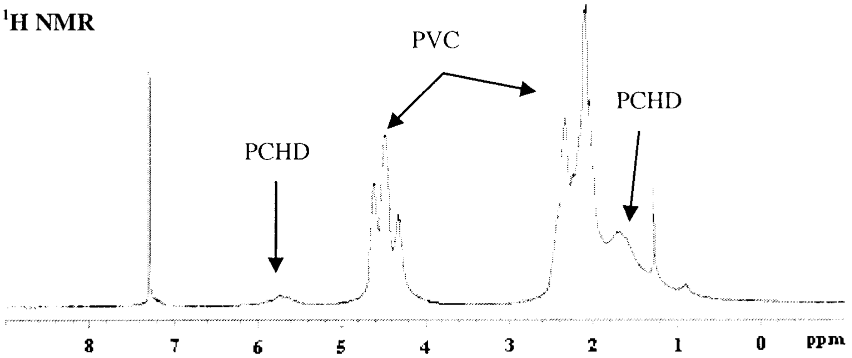


Figure 2. ^{1}H NMR spectrum of PVC-*g*-PCHD.

Table III. The effect of temperature on grafting of 1,3-cyclohexadiene from PVC

Temp.	G_{eff}	G_{PCHD}	$M_{n,PVC\text{-}g\text{-}PCHD}$	$M_{w,PVC\text{-}g\text{-}PCHD}$	$M_{n,PCHD}$	Number of double bonds	Number of Branches
°C	%	%	10^{-3} g/mole				
20	12.1	8.5	40.0	77.0	4.0	48	1.0
-10	18.2	10.5	40.9	77.0	5.0	54	0.9
-30	29.1	15.5	42.6	76.3	7.1	75	0.9

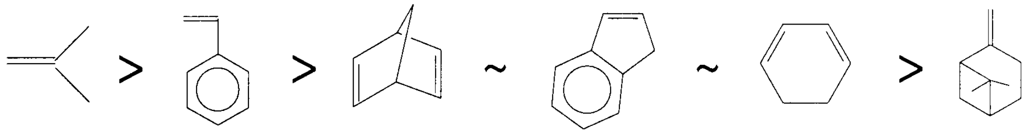
C. The Effect of Temperature on the Molecular Weights of PNbd, PInd, and PCHD

The examination of activation enthalpy difference (ΔH) has given valuable clues in regard to the mechanism of cationic olefin polymerization[12]. To gain insight into the mechanism of grafting of Nbd, Ind, and CHD from PVC, and into the mechanism of polymerization of these monomers in general, we have determined the ΔH values.

Figure 3 shows the log M_n versus 1/T obtained by using the data in Table I-III. The Arrhenius plots are linear in the 20 to –50 °C range and the slopes of the lines yield the following values:

$\Delta H_{Mn,PNbd}$ = -1.7 kcal/mol (-7.1 kJ/mol)
$\Delta H_{Mn,PInd}$ = -1.4 kcal/mol (-5.8 kJ/mol)
$\Delta H_{Mn,PCHD}$ = -1.6 kcal/mol (-6.6 kJ/mol)

Such values have not been determined for these monomers. The temperature effects are similar but much weaker than that observed with isobutylene ($\Delta H_{Mn,PIB}$ = -6.8 kcal/mol (-28.5 kJ/mol)), styrene ($\Delta H_{Mn,PSt}$ = -3.9 kcal/mol (-16.3 kJ/mol)), however, is more pronounced than that with β-pinene ($\Delta H_{Mn,P\beta P}$ = -0.5 kcal/mol)[4]. Evidently, the effect of temperature on the molecular weight of these olefins follows the following sequence:



It is too early to speculate on the interpretation of this sequence.

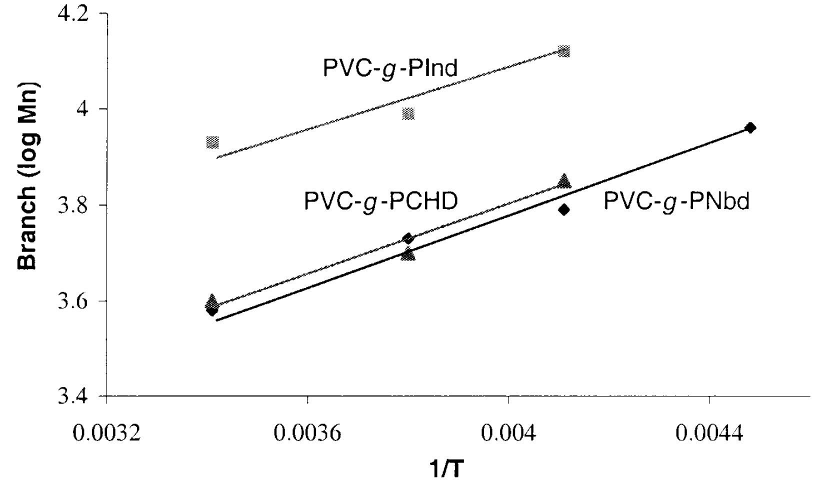


Figure 3. The effect of temperature on the branch molecular weight of PVC-*g*-PInd, PVC-*g*-PNbd, and PVC-*g*-PCHD.

Conclusions

A series of novel graft copolymers PVC-*g*-PNbd, PVC-*g*-PInd, and PVC-*g*-PCHD have been prepared. The synthesis strategy is straightforward and concerns the cationic polymerization initiation of Nbd, Ind, and CHD by the PVC/Et_2AlCl combination. The grafts have been characterized by solvent extraction, T_g, and NMR spectroscopy. The effect of temperature on grafting parameters was studied in the 20 to –50 °C range.

Acknowledgements.

This research was supported by a grant of the National Science Foundation (DMR-9988808) and EPIC. We are grateful to The Geon Company for a PVC sample.

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