

蚕丝辐射接枝丙烯腈*

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摘 要 以氯化锌水溶液为溶剂,用钴-60 γ 射线引发蚕丝均相溶液接枝丙烯腈.研究了辐射吸收剂量、剂量率、铜离子浓度、蚕丝浓度和单体浓度及“后效应”对单体转化率、接枝率、接枝效率、接枝链分子量的影响;研究发现初始接枝效率主要取决于 $[S]_{\text{总}}/([S]_{\text{总}} + [M]_{\text{总}})$,接枝效率随吸收剂量增加而增加;铜离子的存在使接枝链分子量下降,而对接枝率和接枝效率影响不大;用IR、TGA、DTA等多种方法对接枝物进行了表征,表明蚕丝接枝上聚丙烯腈后,其热学性能有较大提高.

关键词 蚕丝,丙烯腈,接枝共聚,辐射引发

蚕丝是一种蛋白质纤维,由于其众所周知的优异性能,使其成为重要的天然纤维之一,在国民经济中起着重要的作用.我国是蚕丝生产大国,生产过程中产生的废丝得不到有效利用,浪费很大,如何变废为宝,已成为人们研究的热点.目前,有关蚕丝综合利用的产品,包括衣料在内有几十种产品,如医学用品、食品和化妆品等.接枝共聚法是改善蚕丝纤维粘弹性、抗水性、染色性、尺寸稳定性等性能的有效方法.绝大多数接枝体系为异相接枝^[1~9],但也有少数学者采用均相接枝^[10,11].本文着眼于废丝的开发利用,使之再生为良好的纤维,采用氯化锌水溶液为溶剂,将丝素蛋白与丙烯腈单体溶为均相体系,用钴-60 γ 射线辐射引发,使蚕丝接枝上聚丙烯腈(PAN).接枝产物纺丝后的织品热稳定性、抗菌性提高,同时又可保持丝织物的属性.

1 实验部分

1.1 原料及试剂

蚕丝料,安徽丝绸厂下脚料,使用前经0.4%肥皂水和0.05%碳酸钠水溶液洗涤.丙烯腈(AN),A.R,北京化工厂,使用前常压蒸馏,收集77~77.5℃馏分.盐酸,A.R,北京化工厂.醋酸,A.R,北京化学试剂厂.氯化锌,A.R,徐州化学试剂厂.硫酸铜,A.R,广州化学试剂厂.DMF,A.R,上海试剂一厂.钴-60 γ 放射源,6万居里,中国科学技术大学.红外光谱仪,Perkin-Elmer577型.热释重分析仪,WRT-3型.差热分析仪,CRY-2型.

1.2 接枝共聚实验方法

称取一定量的废蚕丝,浸入60%氯化锌水溶液,在70℃下溶解,冷却后加入AN,搅拌均匀后倒入辐照瓶,将辐照瓶放入钴源室预定位置,辐照一定时间后取出.

1.3 单体转化率的测定

称取产物100g,在干燥洁净的玻璃板上流延成膜,用大量水清除氯化锌,共聚产物也随之凝聚为冻胶状.将薄膜从玻璃板上揭下,浸入2%醋酸溶液中,除去因水稀释使pH增大而引起氯化锌水解生成的氧化锌沉淀,在真空烘箱中烘至恒重.

$$\text{单体转化率}(\%) = (W_2 - W_1) \times 100 / W_3$$

式中 W_1 为100g原溶液中溶解的丝重, W_2 为100g共聚物溶液成膜干重, W_3 为100g原反应液中丙烯腈重.

1.4 接枝率的测定

将上面处理得到的膜浸入DMF中萃取48h,除去PAN均聚物.萃取后的产物在真空烘箱中50℃下烘干至恒重(W_4).

$$\text{接枝率}(\%) = (W_4 - W_1) \times 100 / W_1$$

1.5 接枝效率的测定

$$\text{接枝效率}(\%) = (W_4 - W_1) \times 100 / (W_2 - W_1)$$

1.6 接枝链PAN分子量的测定

将接枝物浸入6mol/L盐酸中,在95℃下水解2h,洗涤烘干后用玛瑙钵研成粉末,用过滤DMF在40℃下溶解,准确配成浓度为0.2g/dL的溶液,用乌氏粘度计在30℃下测其特性粘数

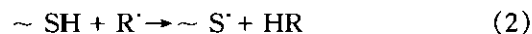
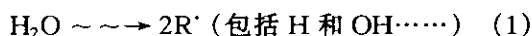
$[\eta]$, 由公式 $[\eta] = 3.92 \times 10^{-4} [M_n]^{3/4}$ 计算接枝链 PAN 的分子量^[10].

2 结果与讨论

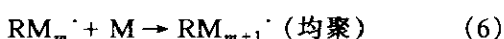
2.1 接枝机理

γ 射线辐射引发蚕丝接枝 AN 的机理可描述如下

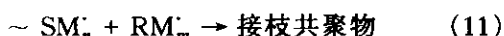
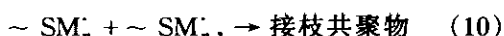
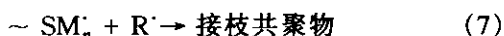
链引发:



链增长:



链终止:



其中 $\sim \text{SH}$ 为蚕丝蛋白质, H 为可被自有基夺取的活泼氢, M 为单体.

2.2 剂量和剂量率对单体转化率的影响

转化率随辐照时间增加而增加, 并到一定剂量后趋于平台, 且在相同辐照时间下, 剂量率愈高, 转化率亦愈高(图 1). 这是因为剂量率高则单位时间内产生的自由基浓度就高, 反应速度快.

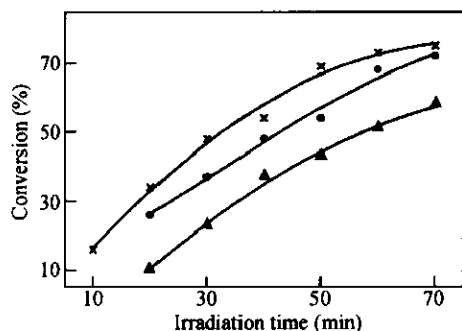


Fig. 1 Conversion curves for various dose rate
 Δ $D = 3.16 \text{ Gy/min}$, $\bullet$ $D = 6.30 \text{ Gy/min}$, $\times$ $D = 23.32 \text{ Gy/min}$
 $[\text{Silk}] = 4 \text{ g/100g solvent}$, $[\text{AN}] = 8.866 \text{ g/100g solvent}$;
 $T = 25^\circ\text{C}$

2.3 剂量和剂量率对接枝率及接枝效率的影响

接枝率随剂量和剂量率的变化及其原因与单体转化率相似(图 2). 从图 3 可知, 接枝效率随辐照时间增加而增加, 可归结为反应(11)所造成; 初始接枝效率约为 31%, 等于 $W_1/(W_1 + W_3) = 4/(4 + 8.86)$, 这意味着引发反应(2)和(4)为扩散控制, 故 $k_2 = k_4$; 相同辐照时间下, 剂量率高接枝效率亦高, 可归结为单体的相对转化率高, 反应(11)快; 相同剂量下, 剂量率低, 接枝率和接枝效率高.

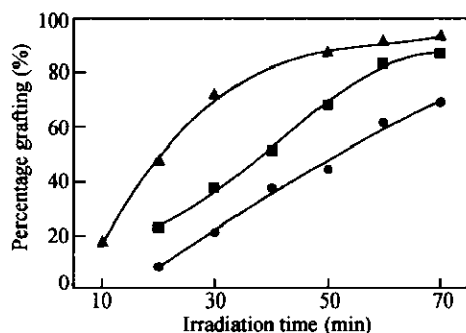


Fig. 2 Percentage grafting curves for various dose rate
 $\bullet$ $D = 3.16 \text{ Gy/min}$, $\blacksquare$ $D = 6.30 \text{ Gy/min}$,
 $\blacktriangle$ $D = 23.32 \text{ Gy/min}$
 $[\text{Silk}]:[\text{AN}]:[\text{Solvent}] = 4:8.86:100$; $T = 25^\circ\text{C}$

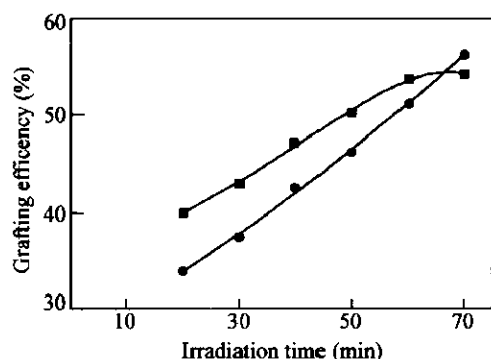


Fig. 3 Grafting efficiency curves for various dose rate
 The conditions are the same as Fig. 2.

2.4 剂量和剂量率对接枝链分子量的影响

在本研究的剂量范围内, 相同剂量率下, 随辐照剂量增加接枝链分子量下降; 剂量率高接枝链分子量低(图 4). 从理论上讲, 接枝链分子量主要取决于链增长反应(5)和链终止反应(7), $M_n \propto k_5[M]/k_7[\text{R}']$, 随辐照时间增加 $[\text{M}]$ 下降, M_n 下降, 剂量率增加 $[\text{R}']$ 增加, M_n 下降.

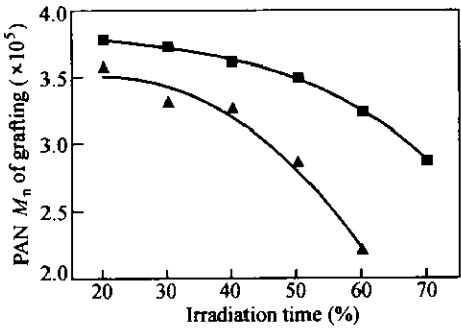


Fig. 4 PAN molecular weight of grafting curves for different dose rates
■ $D = 3.16\text{Gy/min}$, ▲ $D = 6.30\text{Gy/min}$; The other conditions are the same as Fig. 2.

2.5 溶剂中铜离子浓度对接枝共聚的影响

由于废丝中含有微量 Cu^{2+} (4.6×10^{-6}) 和 Fe^{3+} (58×10^{-6}), 高于纯净丝素中 Cu^{2+} 的 1.33×10^{-6} 和 Fe^{3+} 的 8.56×10^{-6} , 故研究这些离子对接枝共聚的影响十分必要. 从图 5 中可看到, 体系中加入铜离子后, 接枝链分子量随铜离子浓度增加而下降, 而对单体转化率和接枝率影响不大 (表 1). 说明铜离子主要是起链转移的作用. 另外, 研究表明, 铁离子对接枝共聚的影响与铜离子类似. 可能的影响机理如下:

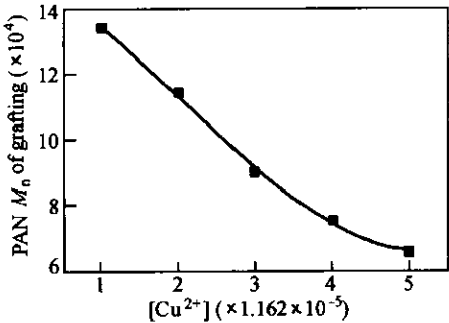
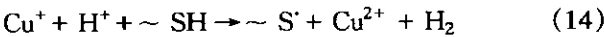
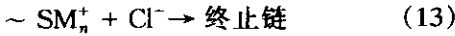
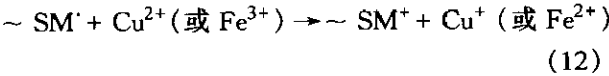


Fig. 5 Effect of copper ion concentration on grafting chain molecular weight
 $D = 6.30\text{Gy/min}$; $t = 30\text{min}$; The other conditions are the same as Fig. 2.

2.6 单体和蚕丝浓度对接枝共聚的影响

前已叙及, 接枝效率主要由反应(2)和(4)决

Table 1 The effect of copper ion concentration on conversion and percentage grafting

$[\text{Cu}^{2+}] (\times 10^{-6})$	11.62	23.24	34.86	46.48	58.1
Conversion (%)	45.0	46.1	45.8	46.5	44.6
Percentage grafting (%)	36.8	37.5	37.0	38.0	36.4

The same conditions as Fig. 5

定, $E_g = R_2 / (R_2 + R_4)$, 对于扩散控制机理, $k_2 = k_4$, 上式可写成:

$$E_g (\%) = [S] \times 100 / ([S] + [M])$$

$[S]$ 可认为是常数, $[S] = [S]_0$. 所以, 接枝效率随蚕丝浓度增加而增加 (图 6), 随单体浓度增加而下降 (图 7).

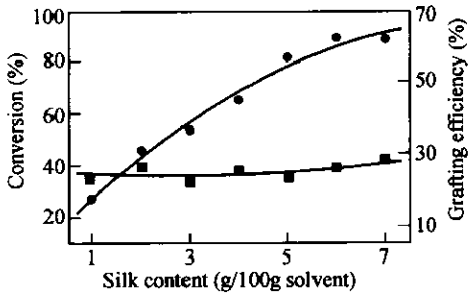


Fig. 6 Conversion and grafting efficiency versus silk content

$[\text{AN}] = 8.866\% (\text{W/W})$; $D = 6.30\text{Gy/min}$;

Irradiation time: 30min, $T = 25^\circ\text{C}$

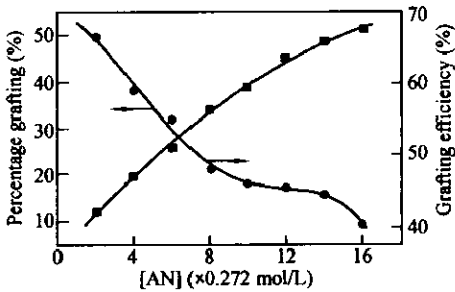


Fig. 7 Percentage grafting and grafting efficiency versus monomer content

$[\text{Silk}] = 4\% (\text{W/W})$; $D = 6.30\text{Gy/min}$; Irradiation time: 30min; $T = 25^\circ\text{C}$

同理, 接枝率可写成:

$$G (\%) \propto [M] / ([M] + [S])$$

则接枝率随单体浓度增加而增加 (图 8), 而随蚕丝浓度增加而下降 (图 8).

另外, 接枝链分子量随蚕丝浓度增加而下降 (图 8), 这可能是由于蚕丝浓度增加使反应(2)加

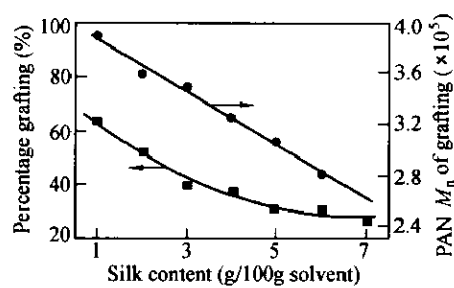


Fig. 8 Percentage grafting and molecular weight of grafting chain versus silk content
[AN] = 8.866% (W/W); D = 6.30Gy/min;
Irradiation time:30min; T = 25℃

快,导致初始自由基相互偶合终止减少,使总自由基浓度增加,由于 $M_n \propto k_5[M]/k_7[R^{\cdot}]$,故 $[R^{\cdot}]$ 增加,分子量下降,这亦解释了接枝链分子量随单体浓度增加而增加(图9),至于当单体浓度进一步增加使分子量下降,则可能是由于单体浓度增加使体系粘度下降, k_7 增加所致。

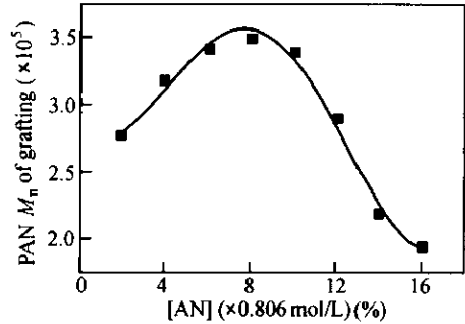


Fig. 9 Molecular weight versus monomer content
The same conditions as Fig. 7

2.7 辐射后聚合对接枝共聚体系粘度的影响

图10是落球粘度法测得的共聚后不同存放时间体系粘度的变化.从图中看到,在起初的两个小时内,体系粘度增加较快,之后变化逐渐变小,这是由于接枝共聚体系粘度较大造成大分子自由基双基碰撞终止困难,寿命增加,停止辐照后自由基依然存活,并可继续引发接枝或聚合,故而体系粘度在相当长的时期内不断增加.这种后聚合效应约有2~3h.

2.8 接枝共聚物表征

2.8.1 溶解性能 将蚕丝和接枝物分别放入55% CaCl₂ 溶液中,发现蚕丝溶解,而接枝物不溶;再将PAN和接枝物分别放入DMF中,发现PAN溶解,而接枝物不溶.说明确有接枝物生成。

2.8.2 IR 光谱 从图11曲线a可看到,在2200cm⁻¹处有一C≡N的强吸收,而曲线b没有,证明蚕丝确实接上了PAN.

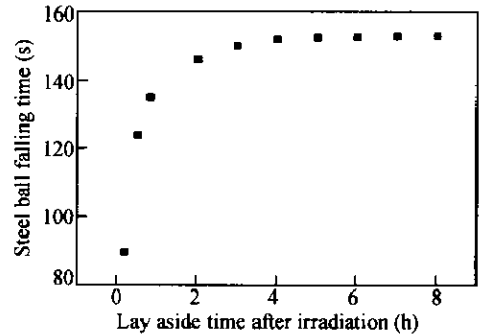


Fig. 10 The influence of “post effect” on viscosity of grafting copolymerization product
[Silk] = 4% (W/W), [AN] = 8.866% (W/W); D = 6.30Gy/min; Irradiation time:30min, T = 25℃

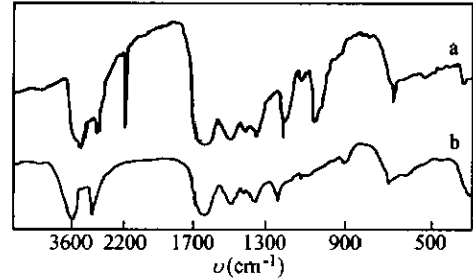


Fig. 11 IR spectra of silk and silk-g-PAN
a) Silk-g-PAN; b) Silk

2.8.3 热失重分析(TGA) 从图12中三条曲线的比较可以看到,接枝物的热失重速度比废丝和PAN都慢,且热失重的温度最高,PAN初始热失重温度最低,废蚕丝的初始热失重温度居中.说明接枝物的热性能最好。

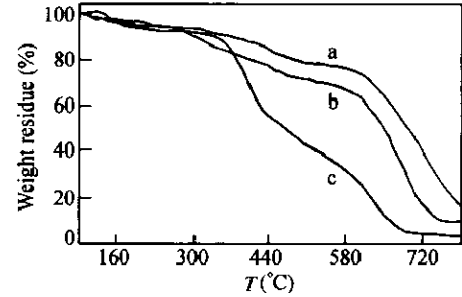


Fig. 12 TGA curves of silk, PAN and silk-g-PAN
a) Silk-g-PAN(percentage grafting:37.1%); b) PAN;
c) Silk

2.8.4 差热分析(DTA) 接枝物只在284℃有

一个吸收峰,而蚕丝与 PAN 混和物在 275.8℃ 和 328℃ 有两个吸收峰,说明分离出来的接枝物是不同于蚕丝与 PAN 混和物的新型物质.

从以上实验结果和讨论可以看到,废蚕丝均相辐射接枝 AN 可以得到性能优良的接枝物,使

废丝得到再生.为满足工业应用的需要,将辐照后的接枝液直接纺丝,得到了强度较好的改性蚕丝,相信适当改变接枝条件和配方,能够制备出一种适合国民经济需要的再生蚕丝,既减少了蚕丝的浪费,也满足了日益增长的消费需求.

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RADIATION GRAFTING OF ACRYLONITRILE ONTO SILK FIBERS

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Abstract To synthesize novel modified fibers from waste silk fibroin, gamma-ray induced graft of acrylonitrile onto silk fibroin in the solution of 60% ZnCl_2 was carried out. The effects of absorbed dose, dose rate, copper ion, silk fibroin contents, monomer concentrations and "post effect" on monomer conversion, percentage grafting, grafting efficiency and average molecular weight of grafting polymer were examined. The grafting products were characterized with IR, TGA, DTA and other methods. It was found and discussed that the initial grafting efficiency is mainly determined by $[S]/[S] + [M]$, where $[S]$ and $[M]$ are the concentrations of silk fibroin and monomer, respectively. Furthermore, the graft efficiency increases with the increase of absorbed dose. It was noticed that the existence of Cu^{2+} has a strong inhibition effect on the molecular weight of grafted chain, and almost no effect on percentage grafting and grafting efficiency. The thermodynamic properties of grafting products were much better than those of natural silk.

Key words Silk, Acrylonitrile, Grafting copolymerization, γ -Radiation induced